STUDY OF ECOLOGICAL RISK ASSESSMENT OF PAHS AND PHENOLS IN PRODUCED WATER AFTER PARTITIONING IN THE WATER PHASE

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Abstract

The impact of produced water from oil and gas operations is not only a function of its chemical composition but also of the receiving environment (e.g. marine versus freshwater organisms, high energy versus low energy water etc...). The resulting toxicity of produced waters is related to chemical compositions, and varies widely from nontoxic (LC_{50}>100 % whole effluent) to moderately toxic (LC_{50}<1 % whole effluent). The impact of produced water tends to be chronic rather than acute and therefore determining the agents in the produced water with the greatest impact has proved difficult, particularly in offshore operations where dilution is rapid. However, the polycyclic aromatic hydrocarbon (PAH) fraction in the oil present in the produced water has been proposed as toxic agent.

In general, regulations prohibit the discharge of produced water containing more than 40 mg/L of oil. The purpose of this paper is to determine the effect of PAHs and phenols in produced water that tend to partition in the water phase once discharged to the ocean, as these compounds will be more readily bioavailable and therefore toxic. Experiments with produced waters from the Hibernia offshore platform and Terra Nova offshore platforms have been performed at Memorial University. The produced water contains dissolved and dispersed oil. In these experiments, the relative amount of PAH and phenol which partition into the water phase after the dispersed oil was separated, and was measured.

The results were then used to determine what the hazard quotient (HQ) is for each of the identified PAHs and phenols in the water phase. A hazard index (HI) for PAHs and phenols, which is the summation of all hazard quotients, was then calculated. The HI

gives an overview of the worst-case estimated hazard of PAHs and phenols to the marine environment. It was found that there was a strong relation between dispersed oil and the amount of naphthalenes and 4-6 rings PAHs as well as phenols but there was no relation between the amount of dispersed oil in produced water and 2-3 rings PAHs. According to the results of risk assessment for PAHs and phenols, there is no significant hazard from either PAHs or phenols on marine organisms. Also, this study showed the importance of dilution in reducing hazards of produced water in marine organisms. However, it was found there was no significant cancer risk from 4-6 ring PAHs in human.

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List of Symbols

ppt	Part per thousand
ppb	Part per billion
ppm	Part per million
mg/L	Milligram per liter
μg/L	Microgram per liter
m^3/day	Cubic meter per day
pCi/L	Picocurie per liter
Bq	Bequerels (disintegration/sec)
S_o	Concentration of solute in fresh water
S_s	Concentration of solute in salt water
K_s	Setschenow constant for each solute
C_s	Molar salt concentration
Cs	Electrolyte concentration
P	Pressure
R	Gas constant
T	Temperature
BCF	Bioconcentration factor
K_{OW}	Partitioning coefficient
C_o	concentration of tracer in the outlet opening
C	Concentration of tracer measured in the recipient
U	Average current velocity

L	Width of the plume diluted in the seawater
H	depth
Q_O	the release rate through the outlet opening
V	Horizontal diffusion velocity
K_Z	Vertical diffusion coefficient
X	Distance from the source
GM	the geometric mean
EC_{50}	Median effects concentration
LC_{50}	Median lethal concentration
PEC	Time-integrated predicted environmental concentration
PNEC	Time-adjusted predicted no-effect concentration
NOEC	No-observed effect concentration
HQ	Hazard quotient
HI	Hazard index
CR	Cancer risk

Chapter 1

Introduction

1.1 Background of the study

Since the beginning of the 20th century, worldwide production of oil and gas has increased by 100%, in an effort to meet the world's energy demand (Patin, 1999). At the end of the 20th century, however, the oil and gas sources were still only supplying approximately two third of the world's total energy demand despite innovations in renewable energy technologies (Patin, 1999), and the remaining third of the total energy is from different sources of renewable energy such as hydro, solar, wind, wave, wood and coal. To meet all of the demands of the world's increasing population and industrial growth, there is a quest to explore new oil and gas energy sources.

The main three phases in the oil and gas industry upstream activities are exploration, development and production. During production, the main waste generated is produced water. Produced water is the water brought up from the hydrocarbon-bearing strata during the extraction of oil and/or gas, which includes formation water, injected water, small volumes of condensed water, and any chemicals added down hole or during the oil/water separation process (USEPA, 1993). Around 6.91 million m^3 of produced water is discharged to surface waters from the offshore industry per year (Wiedeman, 1996). The average discharge of produced water from a platform is about 1500 tonnes/day (GESAMP, 1993). The percentage of produced water from the reservoir can account for

2% to 98% of the extracted fluids (Stephenson, 1992; Wiedeman, 1996). By 1993, produced water had become the first source of oil discharges to the sea, reaching 585 tonnes (Syvertsen et al., 1996).

The ratio between oil and water in produced water varies widely with time, location and properties of the formation layer. Over the economic life of a typical oilfield, generation of produced water can exceed by ten times the volume of hydrocarbons (Stephenson, 1992). USEPA (1993) estimated the ratio of oil to water in produced water for 30 oil and gas producing platforms to be between 0.1 and 12.6. The amount of produced water can reach 40,000 m^3/day.(Scholten, et al., 2000). In 2000 the amount of produced water from the UK offshore facilities reached to 244 million tons (Ekins, et al, 2005). The amount of produced water from US in 2003 was 745,000,000 barrels/year (NRC, 2003).

Produced water's chemical composition is highly variable and complex in nature. In Norwegian sector, the characteristics and chemical compositions of produced water vary from field to field but the main characteristic of produced water from the offshore fields is high salinity, which can exceed sea salinity, and density of seawater (35ppt, 1.02). It is worth noting that the salinity of produced water can reach up to 300 ppt (Neff, 1997). For example, produced water in Hibernia offshore platform has a specific gravity 1.1325 and salinity 195 ppt (CAPP, 2001). The pH of produced water varies from the beginning of production, when it is slightly acidic, 5-6.5, until it gradually increases to 8 (Hansen, 1994). Produced water contains several different chemical substances such as aliphatic hydrocarbons, organic salts, organic acids, polycyclic aromatic hydrocarbons (PAHs), heavy metals (Barium, Beryllium, Cadmium, Copper, Iron, Lead, Nickel, Silver, Zinc, Mercury (Neff et al., 1989), and radioactive materials such as radium^{-226} (226Ra), and

radium^{-228} (228 Ra), those materials called normally occurred radioactive materials (NORM) (Boesch and Rabalais, 1987).

These waters are treated to satisfy the regulatory standards prior to discharge into the surface waters. However, despite their treatment, produced waters still contain toxic chemicals, which are of environmental concern. There is a concern that the discharging of produced water may be causing contamination in fish and fish habitats (DFO, 2001). In the North Sea, sublethal effects have been observed in both adult fish and larvae at varying distances from some platforms (DFO, 2001) discharging produced water. Ecological risk assessment studies from produced water were performed by Furuholt (1996), Stephens et al. (1996), and Karman et al. (1996) on the basis of contaminants in produced water.

Produced water is quickly diluted even within a 50 m radius from the point of discharge (Furuholt, 1996; Meinhold et al. 1996; Mukhtasor, 2001). Various models, such as CORMIX (the Cornell Mixing Zone Expert System), DREAM (Dose Response Effects Assessments Model), CHARM (Chemical Hazard Assessment and Risk Management), have been proposed to compute the dilution based on effluent and ambient properties.

PAHs are one of the main concerns of this study. PAHs are trace contaminants of marine sediments worldwide. They are increasing frequently as major contributors to the hazard to aquatic life of contaminated sediments, especially for areas that are closed to human activities (Neff, 1979, 2002).

PAHs are in the organic fraction of sea aerosols (Preston et al., 1992). PAHs can be considered as anthropogenic pollution by hydrocarbons indicators for the marine

environment (Patin, 1999). The amount of PAHs in produced water ranges from 5000 up to 24,000 kilograms/ year. PAHs tend to bioaccumulate in the marine environment and are very toxic (Hawboldt et al., 2006). The concentration of PAHs in produced water is 1308 mg/l and in sea water is 9-45 ng/l. Not all PAHs are carcinogenic but the strongly carcinogenic PAHs are 7,12-Dimethylbenzene[a]anthracene, 3-Methylcholanthrene and Benzo[a]pyrene. The molecular weight of PAH's can be divided into low molecular weight and high molecular weight (Hawboldt, 2007). The low molecular weight of PAHs can represent 95% of their amount in produced water (Niu, 2005). PAHs which have more than three aromatic rings (Johansen et al., 2004) are in the dispersed phase in produced water and the lighter are in the dissolved phase.

The toxicity of PAHs in the water column and sediments depends on its composition and physical form, which depends on the sources of the PAHs and their concentrations (Neff, 2005).

The sources of PAHs in the marine environment are natural oil seeps, erosion of coal, peat, oil shale deposits, oil and coal spills, discharge of untreated/treated ballast and bilge water from ships, effluent from oil refineries, oil/water separators on oil and gas platforms, sewage treatment plants, forest and grass fires, and some bacteria (Neff, 1979, 2002 ; National Academy of Science, 1985; Varanasi, 1989). The total amount of PAHs from petroleum alone entering the ocean is 170,000 metric tons/year and this includes 20 to 30 tons of the carcinogenic benzo(a)pyrene (Neff, 1979, 2002). The total amount of PAHs from all sources is 230,040 metric tons/year including 700 tons of benzo(a)pyrene (Neff, 2002). Tripp et al. (1981) mentioned that urban coal particles could also be a source of PAHs to the marine environment. Petroleum, however, is considered as the

main source of PAHs in the marine environment (Neff, 1979, 1990, 2002). The most acute sources of PAHs in marine environments are oil spills but their effects are localized and in small area with respect to the fossil fuel input (Farrington, 1978). The main source of phenanthracenes, perylene, pimanthrene, tetra- and pentacyclic PAH are from the diagenic and biogenic processes (Whitehouse, 1983).

Some PAHs, such as Pyrene and anthracene, are always in a liquid phase and not in a gas phase (Patin, 1999), and this leads them to stay in the water column, where they can be easily oxidized and can transform to other harmful compounds but at a lower toxic level (Neff, 1988). The toxicity of PAHs and Alkylephenol have an acute and chronic toxicity in produced water (Frost et al., 1998).

Phenols are the second main concern in this study. Phenol, alkyl phenols, and to a lesser extent halogenated phenols, are natural components of the environment (Buikema et al., 1979). Phenol is an important chemical intermediate in the manufacture of a wide variety of synthetic organic materials. Phenols are present in crude petroleum at low concentrations. Usually, phenols concentrations are lower in refined petroleum, such as diesel fuel. The most abundant phenols in many crude oils are the C_2 through C_9 alkyl phenols.

However, phenol solubility decreases with increasing alkylation. Thus, produced water rarely contains detectable concentrations of the more highly alkylated phenols. The main concern over phenols is their effect of mimicking the female sex hormone estrogen in fish, especially $C_8 - C_9$ phenols (Ekins and Vanner, 2005). Phenols, however, were found to have no effect in the reproduction of cod in the North Sea due to the discharge of produced water (Myhre 2004). Phenol in produced water discharged from the platform is

diluted in the receiving waters by 10,000-fold within 10 m and by 20,000-fold at a distance of 500 m from the discharge (Neff, 2002).

1.2 Scope and purpose of the research

This research is to study partitioning of produced water and then apply various components of ecological risk assessment for PAHs and phenols in the marine environment to determine associated risk. The major components of ecological risk assessment include problem formulation, selection of endpoints, conceptual models (characterization of exposure, and ecological effects) risk characterization, and risk quantification with aquatic ecological risk assessment model (Mukhtasor, 2001). Further, human risk assessment is performed for PAHs, as well as the calculation of hazard quotient, hazard index, and cancer risk. This thesis focuses on the above components of ecological risk assessment with relevance to produced water discharges in the marine environment.

The major objectives of this study are as follows:

- To perform an ecological risk assessment for PAHs and phenols after conducting an experiment on partitioning in the marine environment.
- To study dilution effects using CHARM model.
- To conduct the human risk assessment.

1.3 Organization of the thesis

Chapter 1 explains the scope and objectives of the research and the organization of the thesis. Chapter 2 covers the theoretical background of the research and provides information about characteristics of produced water compositions such as PAHs and phenols. The main focus of chapter 2 is to illustrate the literature related with ecological risk to the marine environment. Chapter 3 describes the experimental work of partitioning of produced water and covers the results of the analysis and discusses these results. Chapter 4 develops a methodology for ecological risk assessment due to toxicological effects of PAHs and phenols on fish and also on humans. The analysis is performed based on the US. EPA (1998) ecological risk assessment framework. All components of ecological risk assessment are applied in this chapter, such as problem formulation, analysis phase and risk characterization. Chapter 5 discusses the conclusions of this research. For future research, recommendations are provided based on the results obtained.

Chapter 2

Characterization of Produced Water

2.1 Introduction

This chapter discusses sources, components, characteristics, and volume of produced water. It focuses on the physical and chemical properties of polycyclic aromatic hydrocarbons and phenols. Also, some properties, such as solubility and partitioning of polycyclic aromatic hydrocarbons, will be discussed in detail. The degradation and sources of polycyclic aromatic hydrocarbons and phenols in the marine sediments will be discussed. Some dilution models for produced water will also be presented.

2.1.1 Sources of produced water

Petroleum and natural gas may be accumulated over millions of years in porous sediments trapped between layers of impermeable rock deep within the earth (Collins, 1975). Water can be trapped with the petroleum and natural gas. This water is as old as the fossil fuel in the reservoir, and is called formation water or connate water (Neff, 2002). Another way in which water can enter the well is by injection into the injection well to displace the oil into the production wells. Produced water can be defined in this way the water (brine) is brought up from the hydrocarbon bearings strata during the extraction of oil and gas and can include formation water, injection water, and small

volumes of condensed water and trace amounts of treatment chemicals" (Neff et al., 1987; Black et al., 1994;Patin, 1999).

Before refining the oil or processing the gas the water should be removed from the oil in the platform or transferred by pipeline to the shore to be treated or re-injected again into the well. The produced water should be treated to meet the regulations before discharging it in the ocean. The following table shows regulation of oil and grease in produced water.

Table 2.1: Regulation of oil and grease in produced water

Daily maximum	Monthly average	Country	References
42 ppm	29 ppm	USA	(Otto and Arnold, 1996; Veil, 1997)
30 ppm	50 ppm	Australia	(Black et al., 1994)
NA	40 ppm	The North Sea, Mediterranean Sea, the Arabian Gulf, and Asia	(Ray, 1996)
40 ppm	-	Canada	CCME, 1999)

2.1.2 Chemicals

Some chemicals can be added to enhance the efficiency of oil/water/gas separation. Although with all of these chemical, which are used in the separation of oil/gas/water, the efficiency is not 100 percent efficient. Other chemicals are added to prevent corrosion, foaming, scale formation, hydrogen sulfide formation, and bacterial growths (Hudgins,

1989, 1991, 1992). Treated produced water that is discharged into the ocean still has a small amount of hydrocarbons, other organic chemicals, dissolved salts, and heavy metals (Neff, 2002). A certain amounts of these chemicals remain in the oil phase but still some amounts are water soluble, and then remain with produced water and are discharged into the ocean with it (Neff, 2002). Table 2.2 shows the amount of production chemicals which remain in the produced water at the North Sea platforms.

Table 2.2 Percentage of chemicals remaining in produced water in North Sea platforms (van Hattum et al., 1992; Ynnesdal and Furuholt, 1994; Hudgins, 1994)

Production chemicals	19%
Emulsifiers, oil removing agents, surfactants, and scale inhibitors	50%
Corrosion inhibitor, oxygen scavengers, emulsion breakers, defoamers, and gas treatment agents.	<20%

2.1.3 Biocides

Biocides are added to the water treatment system for produced water for many reasons, such as re-injection and use to control sulfide production by anaerobic arachea and bacteria in the production stream. The biocides, such as hypochlorides, when they are reacting with organic matters, are easily destroyed (Hudgins, 1991).

Corrosion inhibitors may be water soluble or oil-soluble. In the North Sea, most corrosion inhibitors are oil-soluble and a small amount remains in the water phase (Neff, 2002).

2.1.4 Scale inhibitors

Scale inhibitors tend to remain in produced water because they are water soluble. Scale inhibitors are used to prevent the formation of barium and calcium scale in inside the pipes and are usually nitrogen-containing phosphate esters (Hudgins, 1991).

Around one-third of the amount of injected gas treating chemicals, which are used to treat gas production streams, is discharged with the produced water. These chemicals, such as methanol and ethylene glycol, are used to prevent gas hydrate formation and they remain in produced water. The amount of production chemicals, which is in produced water on production platforms in the North Sea, is shown in Table 2.3.

Table 2.3 Amounts of production chemicals used on production platforms in the North Sea and amounts discharged with produced water to the ocean or injected into a well (Hudgins, 1994).

Chemical	Used (tones/year)	Discharged	Injected (tones/year)
Biocides	2,584	81	2,446
Corrosion inhibitors	2,471	216	0

Oxygen scavengers	1,277	22	1,241
Scale inhibitors	1,727	1,143	515
demulsifiers	444	9	21
Coagulants/de-0ilers	222	189	17
Antifoam agents	144	0	39
Flocculants	203	108	4
Dispersants	NR	NR	NR
Thinners	NR	NR	NR
Fluid-loss control	103	15	NR
Viscostifier	24	24	NR
Emulsifiers	NR	NR	NR
Surfactants/detergents	24	24	NR
Detergents/cleaning	92	87	0
Gas treatment	9,307	2846	2,800
Paraffin control	202	NR	NR
Other	1219	1184	NR
Total additives	30,038	5936	7078

NR Not Reported

2.1.5 Salinity

Salinity of produced water may range from a few parts per thousand in percentage up to saturated brine 300% (Rittenhouse et al., 1969; Large, 1990). Collins (1975) mentioned

that the salinity of produced water from an offshore platform is higher than the salinity of seawater which is 35%. Table 2.4 lists the salinity of produced waters.

Table 2.4 Salinity of produced waters

Platform	Salinity	References
Gulf of Mexico	50% - 150%	(Hanor et al., 1986; Louisiana DEQ, 1990)
The Central Valley of California, the North Slope of Alaska, coastal Texas, and central Mississippi, U.S.A.	18% up to 320%	(Kharaka et al., 1995).

The salinity of produced water is due to dissolved sodium and chloride, as well as a small amount of calcium, magnesium, and potassium. However, the ion ratios in produced water are different than those in the seawater. The calcium to magnesium ratios in two Indonesian produced waters are 6.3 and 23.5, while the Ca/Mg ratios in three produced waters from The Caspian Sea range from 8.91 to 9.71 (Samedova et al., 1997), compared to oceanic seawater of 0.31(Neff and Foster, 1997). The concentration of sulfate in produced water is higher than that in the seawater. The sulfate concentration in the produced water plays a big role in controlling the solubility and, thereby, the

concentration of several other elements, especially calcium and barium (Neff, 2002). The percentage of salinity and concentrations of some selected inorganic ions in seawater and in produced water is shown in Table 2.5.

Table 2.5 The percentage of salinity and concentrations of selected inorganic ions in typical seawater and in produced water (Neff, 2002).

Chemical	Seawater (mg/L)	World produced water (mg/L)
Salinity	32-36%	3-320%
Sodium	10,560	65-97,000
Chloride	18,900	<5-201,000
Calcium	400	13-118,800
Strontium	13	7-3,200
Magnesium	1,270	4-11,700
Potassium	380	3-6,500
Sulfate	880	<1-1,650
Sulfide	--	0.12-256
Ammonia	--	<0.1-650

From the above table, it can be concluded that the salinity of produced water can be similar to that of seawater salinity or higher. Also, amount of ammonia and sulfide in produced water is variable amounts, which can be less than one up to hundreds of mg/L.

2.1.6 Metals

Several metals in solution are found in produced water. The concentrations of metals in produced water are variable and depend on the age and geology of the formation from which the oil and gas are produced (Collins, 1975). According to Olsen et al.(1995) and Samedova et al.(1997), there is no correlation between concentrations of metals in crude oil and their concentrations in water produced with it.

Some metals, such as vanadium and nickel may be abundant in crude oils but rare in produced water. These metals are present as metal-organic complexes (porphyrins) in the oil and do not partition into the produced water phase in contact with the oil. Biodegradation of nickel prophyrins is responsible for the presence of a huge amount of nickel in some North Sea produced waters (Neff, 2002).

Mercury from cinnabar deposits or complexes with the solid organic phase in the hydrocarbon reservoir may evaporate into natural gas in the formation. It may also condense out of the gas into the produced water when the gas and water are brought to surface temperature and pressure (Battelle, 1994). The concentrations of several metals, which are in produced water, are presented in the following table.

Table 2.6 Concentrations of several metals in produced water from seven platforms in the northwestern Gulf of Mexico and 12 discharges to the Norwegian Sector of the North Sea. Typical concentrations in seawater are included for comparison (Neff, 2002)

Metal	Seawater (μg/L)	Gulf of Mexico Produced water (μg/L)	North Sea Produced water (μg/L)
Arsenic(As)	1-3	0.5-31	0.96-1.0
Barium (Ba)	3-34	81,00-342,000	107,000-228,000
Cadmium (Cd)	0.001-0.1	<0.05-1.0	0.45-1.0
Chromium (Cr)	0.1-0.55	<0.1-1.4	5-34
Copper (Cu)	0.03-0.35	<0.2	12-60
Iron (Fe)	0.008-2.0	10,000-37,000	4,200-11,300
Lead (Pb)	0.001-0.1	<0.1-28	0.4-10.2
Manganese (Mn)	0.03-1.0	1,000-7,000	NA
Mercury (Hg)	0.00007-0.0006	<0.01-0.2	0.017-2.74
Molybdenum (Mo)	8-13	0.3-2.2	NA
Nickel (Ni)	0.1-1.0	<1.0-7.0	22-176
Vanadium (V)	1.9	<1.2	NA
Zinc (Zn)	0.006-0.12	10-3,600	10-340

Stephenson et al. (1994) reported that the concentration of metals in produced water changes gradually over time to be similar of the metal concentrations in the seawater only when the seawater is used to enhance production of oil.

2.1.7 Radioactive materials

Produced water contains several naturally occurring radioactive materials (NORM). Radium-226 (^{226}R) and radium^{-228} (^{228}R) are usually the most abundant. The radioactive decay of uranium and thorium associated with certain rocks and clays in the hydrocarbon reservoir form radium (Reid, 1983; Kraemer and Reid, 1984; Michel, 1990). The half life of ^{226}R is 1,601 years and is an α-emitting daughter of uranium-238 and uranium-234. ^{228}R 's half life is 5.7 years and is a β-emitting daughter of thorium-232. Although the two radium isotopes are from different sources in the geological formation, their concentrations in produced water tend to covary (Fisher, 1995).

Neff (2002) reported that the concentrations of radium^{-226} (^{226}R) and radium^{-228} (^{228}R) increase with the salinity in oil and gas produced waters from the coastal and offshore waters of Louisiana, U.S.A. Concentrations of radionuclides in produced water are presented in the following table.

Table 2.7: Concentration of radium-226 (^{226}R) and radium-228 (^{228}R) in produced waters.

Locations	radium-226 (^{226}R) (pCi/L)	radium-228 (^{228}R) (pCi/L)	references
Texas , USA	0.1 - 5,150	NA	Fisher, 1995
Louisiana Gulf Coast, USA	ND-1,565	ND-1,509	Kraemer and Reid,
Offshore USA Gulf of Mexico	91.2-1,494	162-600	Hart et al., 1995
Santa Barbara Channel, CA	165	137	Neff, 1997c
Cook Inlet, Ak	<0.4-9.7	NA	Neff, 1991a
North Sea	44.8	105	Stephenson et al., 1994
S. Java Sea, Indonesia	7.6-56.5	0.6-17.7	Neff & Foster, 1997
Ocean Water	0.027-0.04	0.005	Santschi & Honeyman, 1989

NA not analyzed, ND not detected, Picocurie/L (pCi/L) (1 pCi = 0.037 bequerels [Bq]; 1 Bq = 1 disintegration/sec).

2.1.8 Oxygen Demand

Oxygen demand in produced water is usually not a concern in offshore discharges (except in peculiar circumstances, such as near shore discharges in shallow waters). Table 2.8 shows the chemical and biochemical oxygen demand of produced water.

Table 2.8 Chemical and biochemical oxygen demand (COD & BOD) of produced water (OGP, 2005)

Produced water (origin)	COD (mg O2/l)	BOD5 (mg O2/l)
Northern North Sea platform	130-2070	-
Central North Sea oil platform	4160 (av.)	465
Central North Sea condensate platform	4508 (av.)	1010
Southern North Sea: 8 gas/condensate platform	400-15800	28-6700
Southern North Sea: 7 gas/condensate and 4 oil platforms	96-3000	-
Oil platforms in US water	100-3000	300-2000

2.1.9 Total organic carbon

The concentration of total organic carbon (TOC) in produced water ranges from 0.1 to 11,000 ppm (Fisher, 1987). It is highly varied from one location to another, as shown in Table 2.9.

Table 2.9 Concentration of TOC in different locations.

Location	**TOC concentration (ppm)**	**References**
North Sea	14- 1,000	Tibbetts et al., 1992; Stephenson et al., 1994
Bass Strait, Australia	15-313	Brand et al., 1989
Gulf of Maxico, USA	68-540	Neff, 1997

Concentrations of DOC (dissolved organic carbon) vary widely from less than 17 to as high as 11,000 ppm in produced water from different formations, or even from produced water within the same basin (Fisher, 1987).

2.1.10 Petroleum hydrocarbons

Petroleum hydrocarbons are the organic components of greatest environmental concern in produced water. Hydrocarbons are organic compounds, which containing only carbon

and hydrogen. Carbons are linked by single or double covalent bonds to form linear, branched, and cyclic hydrocarbons.

Aliphatic hydrocarbons have single bonds between carbon atoms. Aromatic hydrocarbons are composed of six-carbon rings in which the six carbon atoms equally share nine covalent bonds.

Infrared spectrometry is used to measure petroleum hydrocarbons, such as oil and grease content in the produced water which account for 25 to 65 percent of TOC in produced water in Cook Inlet (Lysyj, 1982) and 8.5 to 16 percent of the TOC in produced water samples from the Gulf of Mexico analyzed by Neff, 1989c. Table 2.10 shows the mean concentrations of some main organic fractions in produced water.

Table 2.10: Mean concentrations of the main organic fractions in produced water from three offshore production facilities in the Norwegian Sector of the North Sea. (Strømgren et al. 1995)

Chemical class	Facility 1 (mg/L)	Facility 2 (mg/L)	Facility 3 (mg/L)
Volatile acids (C_1-C_{5+})	817	43	229
Fatty acids (C_8-C_{17})	0.5	0.04	0.03
Phenols	7.8	0.8	2.8
Aliphatic hydrocarbons (C_{12}-C_{35})	4.6	25	14.3

Aromatic hydrocarbons (C_{10}- C_{35})	1.1	4.5	2.0
Total extractable organic matter	831	73	248

McAuliff (1966) and Eastcott et al. (1988) reported that the aqueous solubility of petroleum hydrocarbons decreases as their molecular weight increases. Because the oil/water separator equipment is efficient for removing oil droplets but not dissolved oil from the produced water, most of the petroleum hydrocarbons remaining in the produced water after treatment are low molecular weight aromatic and saturated hydrocarbons that are dissolved in the produced water (Neff, 2002).

2.1.11 Aliphatic hydrocarbons

The amount of monocyclic aromatic hydrocarbons in produced waters is twice the amount of saturated hydrocarbons or alkanes with a molecular weight similar to those in BTEX (benzene, toluene, ethylbenzene, and xylenes (Middleditch, 1981; Sauer, 1981b; Neff et al., 1989c).

BTEX is more abundant than normal paraffins (from n-C_{10} to n-C_{34}) in produced water. The most abundant are the normal alkanes, especially from C_{13} to C_{16}. This is due to the

volatility of the low molecular weight alkanes and the extremely low aqueous solubility of alkanes with more than 16 carbons (Coates et al., 1985). Alkanes have much lower aqueous solubility than aromatic hydrocarbons of similar molecular weight. They are presented in produced water as colloidal forms or associated with dispersed oil droplets.

2.1.12 Volatile hydrocarbons

BTEX (benzene, toluene, ethylbenzene, and xylenes), the one-ring aromatic hydrocarbons and low molecular weight saturated hydrocarbons are the most abundant hydrocarbons in produced water. The range of BTEX in produced water varies from 0.01 ppm to as high as 600 ppm (Neff, 2002).

2.1.13 Natural organic components of produced water

Produced water contains some organic components such as cyclic alkanes, sulfur-nitogen, and oxygen substituted hydrocarbons. McAuliffe (1966) reported that these chemicals are more water-soluble than the normal or branched alkanes or unsubstituted hydrocarbons of similar molecular weight. Decalin is a cyclic alkane, composed of two conjugated saturated six-member carbon rings. Benzothiophene and dibenzothiophene are the most abundant sulfur heterocyclic compounds in produced water. Roe Utvik (1999) reported that this compound was found in several North Sea produced waters and in three produced waters from Indonesia.

2.2 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are called polynuclear aromatic hydrocarbons, which are composed of two or more fused benzene rings (Neff, 1979). PAHs consist of two or more fused benzene rings and can reach to nine or more aromatic rings in rasin-asphaltene (Neff, 1979).

PAHs are non-volatile hydrocarbons, have high molecular weights and are susceptible to the photo-oxidation process in surface waters (Lee et al, 1978; Southworth, 1979; Atlas et al, 1981; Herbes, 1981; Mill et al, 1981; Pattan et al, 1981).

PAHs have a relative persistence, mutagenic potential and are carcinogenic (Dunham, 1972; Freudenthal and Johne's , 1976).

The average concentration of total dissolved plus particulate PAH in the Atlantic Ocean is 0.63 ng/l (part per trillion) (Lipiatou et al, 1997). Table 2.11 shows the average concentrations of PAHs in the North Atlanic Ocean.

Table 2.11: PAH concentrations in the dissolved and particulate fractions of surface waters of the North Atlantic Ocean (Lipiatou et al, 1997; Neff, 2002)

Compound	Dissolved, ng/l	Particulate, ng/l
Phenanthrene	0.4	0.0018
Fluoranthrene	0.11	0.0019
Pyrene	0.074	0.0013
Benz[a]anthracene	0.006	0.0005
Chrysene= triphenylene	0.002	0.0018

Benzofluoranthenes	0.0075	0.0025
Benzo[e]pyrene	0.0016	0.0005
Benzo[a]pyrene	0.0015	0.0005
Benzo[ghi]perylene	0.0004	0.0005
Indeno[1,2,3-cd]pyrene	0.0004	0.0005
Total PAHs	0.62	0.012

2.2.1 Type and sources of PAHs

There are many types of PAHs will be represented as follow:

- Pyrogentic PAHs mainly contain three or more aromatic rings and the main source of them is the incomplete combustion of the organic material at a very high temperature which could reach to 700 C. Also, they are formed very rapidly (Neff, 1979, 2002).
- Petrogenic PAHs form at moderate temperatures ranging between 100- 300C . The formation is very slow over millions of years. The main source of those compounds is in coal and crude oil which could contain PAHs with amount varying from 0.2 to more than 7 percent (Neff, 2002).
- Diagenic PAHs form rapidly over days or years by certain organic compounds in soil and sediments.
- Biogenic PAHs form from biosynthesis of organisms (Neff, 1979), such as bactaria and fungi and these kind of PAHs are not true PAHs because they contain oxygen or

nitrogen. The biogenic PAHs are not an important source of PAHs in the marine environment (Neff, 2002).

- Anoxic and hypoxic conditions reduce phenols and quinones to parent PAHs (Wakeham et al, 1980).

It is easy to distinguish the different types of PAH by using appropriate analytical methods (Neff, 2002). PAHs with four to six rings are carcinogenic (Neff, 2002).

2.2.2 Sources of PAHs in the aquatic environment

Sources of PAHs in a marine environment are natural oil seeps, erosion of coal and peat, oil shale deposits, oil and coal spills, discharge of untreated/treated ballast and bilge water from ships, effluent from oil refineries, oil/water separators on oil and gas platforms, sewage treatment plants, forest and grass fires, and some bacteria (Neff, 1979, 2002 ; National Academy of Science, 1985; Varanasi, 1989). Neff (1979, 2002) mentioned that the total amount of PAHs entering the ocean is 170,000 metric tons/year from petroleum, alone, and 20 to 30 tons of that are the carcinogenic benzo(a)pyrene. The total amount of PAHs from all sources is 230,040 metric tons/year including 700 tons of benzo(a)pyrene (Neff, 2002). Tripp et al, (1981) mentioned that the urban coal particles could be a source of PAHs to the marine environment. Petroleum is considered as the main source of PAH in the marine environment (Neff, 1979, 1990, 2002). It was found by Laflamme and Hites, 1978; Windsor and Hites, 1979; Gschwend and Hites, 1981, that the concentration of PAHs in the marine environment decreases with increasing distance from urban places.

The human activities (industrial, sewage treatment plants,...etc) could be included as a main source of PAHs, just as crude oil is in the marine environment.

The most acute sources of PAHs in marine environments are oil spills, but their effects are localized and in a small area with respect to the fossil fuel input (Farrington, 1978). The main source of phenanthracenes, perylene, retene, pimanthrene, tetra- and pentacyclic PAH are from diagenic and biogenic processes (Whitehouse, 1983).

2.2.3 Physical and chemical properties of PAHs

2.2.3.1 Solubility

Since many PAHs rank among the most toxic components of crude oil (Ramchandran et al., 2006), PAH solubility is an important feature of produced water. Many studies have been done to discuss the solubility of PAHs in water column, and most data available on the solubility of PAHs in water is for distilled water at 25^0C as in Whitehouse, (1983). Solubility of PAHs varies widely and is affected by many factors, such as temperature, salinity, the combination of different PAHs together, molecular weight of PAHs, pressure, and surfactants. Due to the non-polar hydrophobic nature of the PAHs, they have a low solubility (Neff, 1979).

2.2.3.2 Effect of salinity

Salting-out occurs when solubility and temperature decrease with increasing salt concentration. Salting-in occurs when solubility increases upon the addition of salt.

PAHs solubility in solute solutions could be determined empirically by the Setschenow equation (Setschenow, 1889):

$\text{Log } S_o/S_s = K_sC_s$

Where,

S_o : concentration of solute in fresh water (mol/kg)

S_s : Concentration of solute in salt water (mole/kg)

K_s : Setschenow constant for each solute

C_s : Molar salt concentration (mole/kg)

Whitehouse (1983, 1984) confirmed the effect of temperature that was discovered by May (1978), who found that salinity has less of an effect on solubility of PAHs than the effect of temperature. Also, Whitehouse found the effect of salinity ranged from 0 to 36% and he demonstrated a reverse relationship between salinity and solubility (Varanasi, 1989), and this agrees with salting-out theory. The solubility of PAHs could be twice as high in freshwater as in seawater (Neff, 2002).

A small amount of particulate PAHs could be salting–in to the water column (Whitehouse, 1983; Neff, 1991; Neff and Stubbefield, 1995). This is due to the hydrophobicity of PAHs. The following table will show the effect of salinity on solubility of PAHs in produced water.

Table 2.12: Effect of salinity on solubility of PAHs (Shukla et al., 2007)

PAH	Water soluble fraction (WSF) concentration in ppm		
	WSF (0%)	WSF (15%)	WSF (30%)
Naphthalene	19.9	14.9	11.2
Phenanthrene	0.8	0.6	0.5
Fluorene	1.4	1.26	1.18
Pyrene	o.5	0.42	0.36
Chrysene	0.46	0.40	0.0

The salinity controls PAHs solubility and bioavailability in an aquatic system. The solubility of hydrophobic organic contaminants is low at higher salinities (Schlautman et al., 2004).

The potential risks to aquatic life of PAHs' toxicity are enhanced in lower salinity waters such as estuaries and waters near a coastal zone (Shukla et al., 2007).

2.2.3.3 Effect of temperature

Temperature has an effect on the solubility of PAHs from a two to a five-fold increase of temperature, from 5 to 30°C (May, 1978). Whitehouse (1985) studied the solubility of phenanthrene, anthracene, 1,2-benzanthracene, and benzo(a)pyrene in different

temperatures from 278.6K up to 298.2K at different salinities. The following table shows the effect of salinity and temperature on some PAHs.

Table 2.13 Solubility of PAHs in distilled water and seawater (modified from Neff, 1979)

PAHs	Solubility in distilled water (μg/L)	Solubility in seawater (μg/L)
Naphtalene	12,500a, 22,000b, 31,200c, 31,300d 31,500e, 34,000f @25 oC	22,000 @25oC d, 20 mg/l @22oCe
Phenanthrene	1,080 @25oC h, 423 @ 8.5 oC I , 1,277 @29.9oC j	644 @25oC h
Fluorene	1685@25oC d	0.8f mg/l @22 oC
Phenanthrene	1,002 i, 1,070 d, 1,180 c, 1,600 j @25 oC	0.6 f mg/l@22 oC , 0.71 mg/l d @25oC
1-Methylphenanthrene	269 i @25 oC	0.3 mg/l f@22 oC
Fluoranthene	206k, 236 b, 240 j, 265 a@25 oC	0.1 mg/l f@22 oC
Coronene	0.14e	

[a] Klevens, 1950, [b] Schwarz and Wasik, 1976, [c] Wauchope and Getzen, 1972, [d] Eganhouse and Calder, 1976, [e] Neff, 2002, [f] Rossi and Neff, 1978, [g] Bohon and Claussen, 1951, [h] Eastcott et al., 1988, [i] May et al., 1978a, [j] Davis et al., 1942, [k] May et al., 1978b.

According to Table 2-13, the solubility of the same PAH can differ. This could be due to different methods of measuring (Neff, 1979), to the effect of different PAHs on each other, or to the accuracy of measuring (Klevens, 1950). However, there are some exceptions for this base. For example, 1,2-benzanthracene has a salting-in greater at lower temperature and lower salinity than of low temperature (Whitehouse, 1983). Also, the solubility of naphthalene increases by a factor of 5 when raising the temperature from 20 °C to 60 °C (Feitkenhauer and Markl, 2003). The bioavailability of PAHS does not relate to their solubility (Harayama, 1997). Table 2.14 shows the solubility of naphthalene in distilled water at different temperatures and at different salinities.

Table 2.14: Solubility of naphthalene in distilled water and different salinities at different temperatures (Gold et al. 1989)

Water salinity (ppt)	Temperature C	Solubility (μg/L)
0	44	53,800
	35	37,800
	25	25,900

	14	16,800
	4	11,800
26	44	45,500
	35	32,300
	25	22,000
	14	14,100
	4	10,000
35	44	43,200
	35	30,500
	25	21,000
	14	13,400
	4	9,810
53	44	39,200
	35	28,000
	25	19,100
	14	12,300
	4	8,540

According to the above table, the effect of temperature on solubility of naphthalene is greater than the effect of salinity.

Setschenow constant K_S can be determined by using the following (Gold et. al., 1989):

$K_S = \lim V_i^{\circ} / 2.3\ RT dP_e/dC_s$

Where, Cs is the electrolyte concentration. This equation contains explicitly the pressure (P) exerted by the electrolyte, R is the gas constant = 0.0821 L.atm K^{-1} mol^{-1}, T is temperature.

The above equation shows that the solubility depends on temperature.

The following equation is used to calculate the solubility for PAHs (Mackay et al, 1977):

$R \ln X_2^3 = -(\Delta Hm^{\circ}/T) + (0.000408)(T - 291.15)^2 - c + bT$

Where, X_2^3 is the mole fraction of solute at saturation at absolute temperature T, ΔH_m° is the molar heat of fusion of the pure solid solute at the melting point, and b and c are determined by least-squares fit.

This equation has been found to describe hydrocarbon solubility as well. Table 2.15 shows the solubility of some PAHs at different temperature and different salinities.

Table 2.15: Solubility of some PAHs in different temperatures and different salinities (Whitehouse, 1983):

PAH	Salinity (µg/L)	Solubility (nmole/ l) at different Temperatures ^{0}C					
		4.6	8.8	12.9	17	21	25.3
Phenanthrene (µmole/l)	0	2.01	2.45	3.12	4.04	4.94	6.16
	16.6	1.67	2.16	2.72	3.49	4.35	5.38

	36.6	1.36	1.75	2.21	2.81	3.59	4.54
Anthracene	0	53.9	72.4	99.3	133	181	248
	16.6	46.6	62.8	84.2	113	153	205
	36.5	37.9	50.7	68.4	97.6	131	182
2-methylanthracene	0	-	39.2	50.4	63.9	84	117
	16.8	19.1	26	35.7	47.9	64.7	91.2
	36.5	15.6	19.5	35.7	49.4	70.8	
2-ethylanthracene	0	33.8	40.8	54.1	68	92.6	130
	16.8	25.4	33.8	43.8	57.6	79.1	105
	36.5	18.7	24.5	32.5	43.6	60.9	79.7
1,-benzanthracene	0	21.3	18.9	18.8	20.6	27.6	37.4
	16.8	91.9	60.1	42.2	33.4	38.2	47.5
	36.7	-	-	-	44.5	39.5	41.6
Benz[a]pyrene	0	-	2.64	3	3.74	4.61	6.09
	16.8	-	1.79	2.1	3.02	4.19	5.28
	36.7	-	1.4	2.07	2.5	3.43	4.45

It has been found by Whitehouse (1983) that there is no difference between solubility in distilled water and saline water ranged from zero up to 4 % salinity. Also, there is no difference in solubility of PAHs in saline water ranged from 33% up to 36%. This is verified by Viamajala et al. (2007) who performed solubility tests in distilled water on

phenanthrene, fluorine and fluoranthrene at temperatures ranging from 20oC, 40°C and 60°C.

Increasing temperature has a great effect on thermodynamic properties of PAHs. The Henry's law constant could be determined by thermodynamic as follows: (Reza and Trejo, 2004)

$H_i = K_{H,i}\, V_{m,w} / RT$

Where, H_i is Henry's law constant, $V_{m,w}$ is the molar volume of water, R is the gas constant, T is the temperature.

Activity coefficient for PAHs in water (Sandler, 1999; Reza and Trejo, 2004):

$$\ln \gamma^{\infty}_i X_i = \{\Delta H^{o}_{fus,I}\ (T_{fus,I})\ [1 - T/T_{fus,I}]\}/RT \quad - 1/RT * [\int \Delta Cp_i\, dT + 1/R \int_{T}^{T_{fus,I}} \Delta Cp_i / T\, dT]$$

Where: γ activity coefficient, $T_{fus,I}$ is the melting point temperature, $\Delta H^{o}_{fus,I}$ is the molar enthalpy of fusion at $T_{fus,I}$, and ΔCp_i is the difference in heat capacities between the liquid and solid phases.

According to the above equations, any changes in the temperature will affect the thermodynamic properties of PAHs.

2.2.3.4 Effect of molecular weight

Molecular weight of PAHs has an effect on their solubility; with increasing molecular weight solubility decreases. Due to this fact the tendency of PAHs with large molecular weight to leave the water phase and attach to any solid phase increases (Varanasi, 1989)

Also increasing the number of aromatic rings decreases solubility of PAHs. (Neff, 1979). Although of that the PAHs have a higher aqueous solubility than the alkane which have the similar molecular weight. (McAuliffe, 1966).

The angular PAHs isomers have higher solubility than the linear ones. (Neff, 1979). According to Whitehouse (1983) phenanthrene has solubility 25 times greater than anthracene, we can explain this as follow: Both of phenanthrene and anthracene have three aromatic rings but distributions of them are different in phenanthrene the aromatic rings are an angular shape but in anthrathene are a straight line, i.e distribution of aromatic rings in molecule has an effect on its solubility.

The log S (solubility) of PAHs in water decreases linearly with increasing the length of molecule (Klevens, 1950)

2.2.3.5 Effect of presence of some PAHs together and organic compounds

The solubility of PAHs could be affected by the presence of certain PAHs, for example, naphthalene has no effect when it is present with other PAHs but could increase the solubility of acenaphthalene. The presence of biphenyl and phenanthrene together decreases their solubility (Eganhouse and Calder, 1976). Butyric acids and lactic acids have a great effect on solubility of PAHs, which increase their solubility (Ekwall and

Sjoblom, 1952). Natural waters contain organics, such as humic acid and fulvic acid which act as PAHs'solubilizers (Neff, 1979). Dissolved organic carbon (DOC) increases solubility of PAHs, but when DOC concentration increases up to 14.9 mgC/l it has no effect on some PAHs, such as phenanthrene and enhance solubility of other PAHs as 2-ethylanthracen by 45% and benzo[a]pyrene by 252% (Naes et al., 1998).

2.2.3.6 Effect of alkylation of PAHs

Alkylated PAHs have a lower solubility than the unalkylated parent (Neff, 1979). Despite that the alkylated PAHs have lower solubility than the unalkylated ones, there are some exceptions. For example, benza[a]anthracene has less solubility than methyl or ethylbenz[a]anthracene, and also chrysene has a lower solubility than dimethylchrysene (Davis et al., 1942).

2.2.3.7 Effect of Pressure

Effect of pressure on solubility of PAHs in water, Suzuki et al. (1975) reported that the solubility of naphthalene decreases linearly by increasing the pressure in pure water, but the dissolution process of naphthalene in salt water is not clear. Miller et al.(1998) mentioned although large increases in pressure have a depressing effect on solubilities over the range of pressures (30 to 60 bar), very little change in the solubility of anthracene, pyrene, chrysene.

2.2.3.8 Effect of surfactants

Effect of surfactants that are used in exploration and production of oil and gas have a great effect on increasing or decreasing solubility of PAHs as mentioned by Dar (2007) who used miceller solutions to study their effects on solubility of PAHs in water. The cationic surfactants have more an inhibiting effect on solubility of PAHs than nonionic solutions. Also, the cationic - nonionic binary combinations have greater effect to enhance solubility of PAHs in water than the pure cationic or nonionic surfactants.

2.2.4 Determination of solubility

There are two main methods that are used to determine solubility for hydrocarbons (Whitehouse, 1983):

- Mechanical mixing method (Shake- Flask technique)
- A liquid chromatographic method (Micro-column or Dynamic Coupled Column Liquid Chromatography DCCLC). Table 2.16 shows the differences between DCCLTC technique and shake-Flask technique.

Table 2.16 The differences between the two techniques (Whitehouse, 1983)

DCCLC Technique	Shake-Flask Technique
No supper saturation effects	Supper saturation effects
No solute adsorption onto the walls of analytical equipments	Solute adsorption onto the walls
No sample loss and contamination which occur during organic extraction	Sample loss and contamination
Faster	Slower
Temperature controlled	No temperature controlled

Solubility of PAHs in distilled water was determined by Klevens (1950), who used a very simple method in which the PAHs' crystals had been shaking in 1 liter distilled water for about three months then the aliquots were removed and the concentrations determined by spectra.

2.2.5 Equilibrium partitioning coefficient

Many factors could affect the studying of partitioning of PAHs as physical, chemical, biological, and geological influences (Whitehouse, 1983).

There is an inverse relation between $\log K_{ow}$ and temperature i.e increasing temperature lower K_{ow} due to decreasing of affinity of PAHs for the hydrophobic cell membranes,

resulting in decreasing driving force for absorption of PAHs by the cells (Viamajala et al., 2007; Neff, 2002).

The negative effect of lowering K_{ow} can be offset by the uptake of the microorganisms which possesses an active substrate uptake mechanism and do not depend on the passive sorption process of the substrate (Viamajala et al., 2007).

In general aromatic hydrocarbons are hydrophobic and tend to diffuse down an activity from the water phase into the lipid-tissues of marine organisms (Neff, 1982).

The equation which has been recommended by EPA to be used to determine the relationship between BCF and K_{ow} is Veith and Kosian equation (1983):

$\text{Log BCF} = 0.79 \log K_{ow} - 0.4$

Where, BCF: bio-concentration factor, K_{ow}: partitioning coefficient, 0.79: the slope constant, -0.4: the intercept constant.

This equation was developed by Veith and Kosian (1983) by determining the regression of log BCF in 13 species of freshwater fish versus log K_{ow} for 122 non-polar organic hydrocarbonds, including five PAHs (Neff, 2002).

The partitioning coefficient was determined for eight PAHs (Naphthalene, 1-methylnaphtalene, 2-methylnaphtalene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene) between diesel fuel phase and distilled water phase by the following equation (Lee et al., 1992):

$\text{Log } K_d = -\log S_l - \log(Mw_o/\rho_o)$

Where: K_d : the liquid-liquid partitioning coefficient, Mw_o: the average molecular weight of organic phase, ρ_o: the density of the organic phase, and S_l is the aqueous solubility of the pure liquid solute (mol/l).

This equation can be used only under these conditions (Lee, 1992):

- The solution is ideal
- Pure solute

K_d could also be determined from the following equation: (Lee, 1992)

$K_d = C_o / C_w$

Where C_o is the molar concentration of organic chemical phase, and C_w is the molar concentration of aqueous phase. Table 2.17 will show the values of Log K_d and Log K_{ow} for eight PAHs.

Table 2.17 Log K_d and Log K_{ow} values for eight PAHs (diesel-water phases) (Lee, 1992, Neff, 2002)

Compound	Log Kow	Log Kd
Naphthalene	3.33	3.68
1-methylnaphtalene	3.87	4.3
2-methylnaphtalene	-	4.42
Acenaphthene	-	4.53
Fluorine	4.18	4.48

Phenanthrene	4.57	4.69
Anthracene	-	5.27
Fluoranthene	-	5.29

From the above table, It can be seen that there is a difference between partitioning of PAHs from diesel fuel-water and octanol-water phases. It is very important to study the partitioning of PAHs in different phases.

Temperature and salinity have a great effect on the partitioning of PAHs between water and sediments (Neff, 2002). The sorption of PAHs in sediments increases with increasing of salinity and decreasing temperature. (Neff, 2002). This is consistent with whitehouse's findings (1983).

According to Zhang (1995), increasing partitioning coefficient between organic and water phase in the hydrophobic organic chemicals is due to the increase in the lipophobicity not hydrophobicity.

PAHs do not have certain behavior in partitioning in the marine environment, for example naphthalene, alkylnaphthalene, fluorine, and phenanthrene tend to evaporate from the water column (Neff, 2002) and this is due to their relatively small molecular weight. From this, we can say that the lower molecular weight PAHs tend to partition between water to air. The PAHs with high molecular weights tend to partition between water and solid (sediment) (Neff, 2002). This depends on Henry's law constant. As mentioned by

Neff (2002), with increasing the Henry's law constant the PAHs tend to evaporate and if the constant is low the PAHs tend to precipitate in sediments.

Another factor that can affect the partitioning of PAHs is organic carbon/water partition coefficient which are proportional with K_{ow}.(Neff, 2002).

The pyrogenic PAHs associated with soot in sediments do not partition to water phase, so they have low mobility, low bioavailability, and low toxicity (Readman et al., 1987; McGroddy and Frrington, 1995; Maruya et al, 1997).

2.2.6 Bioaccumulation of PAHs

Bioaccumulation could be defined as "the uptake and retention of bioavailable chemical from any one of, or all possible external sources (water, food, substrate, air). It is the net result of the uptake, distribution, and elimination of a substance in an organism due to exposure in water, food, sediment, and air" (ECETOC, 1996; Neff, 2002). The bioaccumulation occurs when uptake is greater than the loss of the substance from the organisms (Neff, 2002).

Fish can accumulate soluble petroleum hydrocarbons very rapidly (Collier et al., 1996) and the fish that are placed in water contaminated with crude oil will take up dissolved hydrocarbons until the steady state is established between the fish and water (Shukla et al, 2007). The hydrophobic nature of the more toxic PAHs enables them to partition directly from the oil droplets to lipid rich tissues coming into contact with oil droplets. Uptake of soluble PAH may be also be influenced by changes in osmoregulation, if PAHs are taken up across the gills by transport with water (Shukla et al., 2007).

For marine organisms the bioaccumulation for any chemicals in them is measured as a bioaccumulation factor (BAF), which is defined as "the ratio of the concentration of the chemical in the tissues of the organism to its concentration in all ambient environmental compartments in the equilibrium with the organism" (Neff, 2002). Also Farrington and Wastall (1986) defined the BAF as "the ratio of the sum of the uptake rate constants of the chemical from all environmental compartments accessible to the organism to the sum of the release rate constants by active or passive mechanisms from the organism".

PAHs have a low bioavailability due to their limited water solubility or low mass transfer from solid phase to aqueous phase (Hrayama, 1997; Feitkenhaur et al, 2003).

The bioavailability of PAHs could be increased by :

- Oxidative pre-treatments that use Fenton's reagents, such as ozone or peroxide, can break PAHs into more soluble compounds and more bioavailable (Stehr et al., 2001). But the main problem is these soluble compounds are more toxic than the parent PAHs (Kornmuller et al , 1997; Stehr et al., 2001).
- Surfactants can increase concentration of PAHs in solution (Grimberg et al, 1994) but surfactants under various conditions can enhance and inhibit PAH degradation (Rause et al., 1994).
- Rising temperature increases bioavailability and biodegradation of PAHs (Annweiler et al., 2000; Margesin and Schinner, 2001; Feitkenhauer and Markl, 2003; Feitkenhauer et al., 2003) which increases solubility and mass transfer rates of PAHs in aqueous solutions (Viamajala et al., 2007).

2.2.7 Bio-concentration of PAHs

A special case of bioaccumulation is bioconcentration, which is "the uptake and retention of a chemical from water alone" (Neff, 2002). Bioconcentration is easy to be measured and modeled mathematically (Neff, 2002). Bioconcentration is measured by bioconcentration factor (BCF), which is unitless, and could be expressed by the following equation:

$BCF = C_T/C_W = K_1/K_2$

Where,

C_T : the concentration of the chemical in tissues

C_W : the concentration of the chemical in water

K_1 : the uptake clearance (unit mass of chemical/ unit mass of tissue/unit time) which is $time^{-1}$ (Spacie and Hamelink, 1982)

K_2 : the release rate constant, $time^{-1}$

The bioconcentration factor and partitioning coefficient for PAHs are presented in the following table.

Table 2.18 Bioconcentration factor and partitioning coefficient for PAHs (Veith et al, 1983)

PAHs	Log Kow	Log BCF	Species	Time	Tissues	Ref.
Naphthalene	3.59 3.59	2.63 1.9	Fathead Coho Salmon	28D 35D	w. body Muscle	Veith et al, 1979
2-Methylnaphthalene	3.84	2.28	Coho Salmon	35D	Muscle	Roubal et al, 1978
1-Methylnaphthalene	3.84	2.11	Coho Salmon	35D	Muscle	Roubal et al, 1978
Biphenyl	4.09	3.12	Rainbow trout	4D	Muscle	Veith et al, 1979
Fluorene	4.38	3.11	Fathead	28D	w. body	Veith et al, 1979
Phenanthrene	4.46	3.42	Fathead	4D	w. body	Veith et al, 1979

From the above Table every marine organism has it's a different reaction than others for the same PAH, such as Fathead and Coho Salmon with naphthalene.

2.2.8 Degradation of PAHs

PAHs in water and sediments are not persistent. Various natural processes responsible of degradation of PAHs to various polar organic chemicals, and ultimately to carbon dioxide and water. The most important degradative processes for PAHs in the marine environment are photooxidation and biodegradation (Bongiovanni et al., 1989; Ehrhardt et al., 1992).

2.2.8.1 Photooxidation of PAHs

2.2.8.1.1 Overview of general photolysis

Photooxidation reactions upon electronic excitation of the organic substrate imply in most cases an electron transfer from the excited-state (C*) to ground-state molecular oxygen with subsequent recombination of the radical ions or hydrolysis of the radical cation or homolysis to form radicals which then react with oxygen.

$C \xrightarrow{h\nu} C^*$

$C^* + O_2 \rightarrow C^{\bullet +} + O_2^{\bullet -}$

$R\text{-}X \xrightarrow{h\nu} R^\bullet + X^\bullet$

Rate of such a photooxidation upon electronic excitation of the organic substrate depends on the absorption cross section of the medium, the quantum yield of the process, the

photon rate at the wavelength of excitation and the concentration of dissolved molecular oxygen (Kwon et al. 2009).

The ordinary reaction rate can be used to determine kinetics of degradation of PAHs:

$r = dc/dt = -kc^n$

Where r is the reaction rate, c is the concentration of PAH, k is a constant and n is reaction order.

Photodegradation rates of different PAHs vary widely. Many factors affect the degradation rates of PAHs such as concentrations of PAHs and photosensitizers in the oil, and on the physical form of the PAHs assemblage (Mill et al., 1981; Valerio and Lazzarotto, 1985). The dissolved PAHs are more sensitive to photo-oxidation than PAHs bound to soot particles are (Valerio and Lazzarotto, 1985; Kamens et al., 1988). Some PAHs such as naphthalene and alkylnaphthalenes in the maltene fraction of ten crude oils and a moderately-weathered light Arabian crude oil are photo-oxidized rapidly in natural sunlight (Jacquot et al., 1996; Dutta and Harayama, 2000). Phenanthrene, dibenzothiophene, and their alkyl homologues are more recalcitrant (Berthou and Vignier, 1986). Dutta and Harayama (2000) reported that diobenzothiophene and methyldibenzothiophenes in weathered light Arabian Crude oil are not photooxidized during four-weeks exposure to artificial sunlight. Between 16 and 91 percent of the more highly alkylated dibenzothiophenes are photooxidized. Methylphenanthrenes and dimethylfluorenes have a low efficiency of photooxidation. Different monomethyland dimethyl-phenanthrene isomers are photooxidized at widely different rates (Jacquot et al.,

1996). The high molecular weight four- through six-ring PAHs is the most sensitive to photo-oxidation (Mill et al., 1981).

Some polymerization reactions of some PAHs occure due to photooxidation, which produce high molecular weight compounds that are not soluble in either water or oil, resulting in a phase separation in the oil slick (Thominette and Verdu, 1984b; Daling, 1988; Nicodem et al., 1997).

Some lower molecular weight aromatic hydrocarbons, such as phenanthrene, were converted to polar oxidation products that tended to bind tightly, possibly covalently, to the resin/asphaltene fraction. Thominette and Verdu (1984b) identified this fraction probably corresponds to the oil- and water-insoluble fraction. Some of these high molecular weight photooxidation products probably consist of polymerized resin-asphaltene materials.

The most important photochemical reactions for aromatic hydrocarbons in solution in the upper water column are direct photolysis reactions that do not require molecular oxygen (Zepp and Scholtzhauer, 1979; Mill et al., 1981).

Increasing molecular weight increasing sensitivity of PAHs in solution to direct photolysis.

The rate of photolysis of PAHs decreases with increasing depth because of the ultraviolet light intensity decreases logarithmically with depth in the ocean. Under intense sunlight, hydrocarbons in solution can be photooxidized to a depth of about 25 m in clear seawater (Jacquot et al., 1996).

2.2.8.2 Microbial Degradation

Around several production platforms discharging produced water to the North Sea, the rate of microbial degradation of naphthalene in the upper water column, ranges from non-detectable to 19.8 mg/m3/day (Massie et al., 1985).Degradation rate of all PAHs increases with increasing aqueous concentrations.

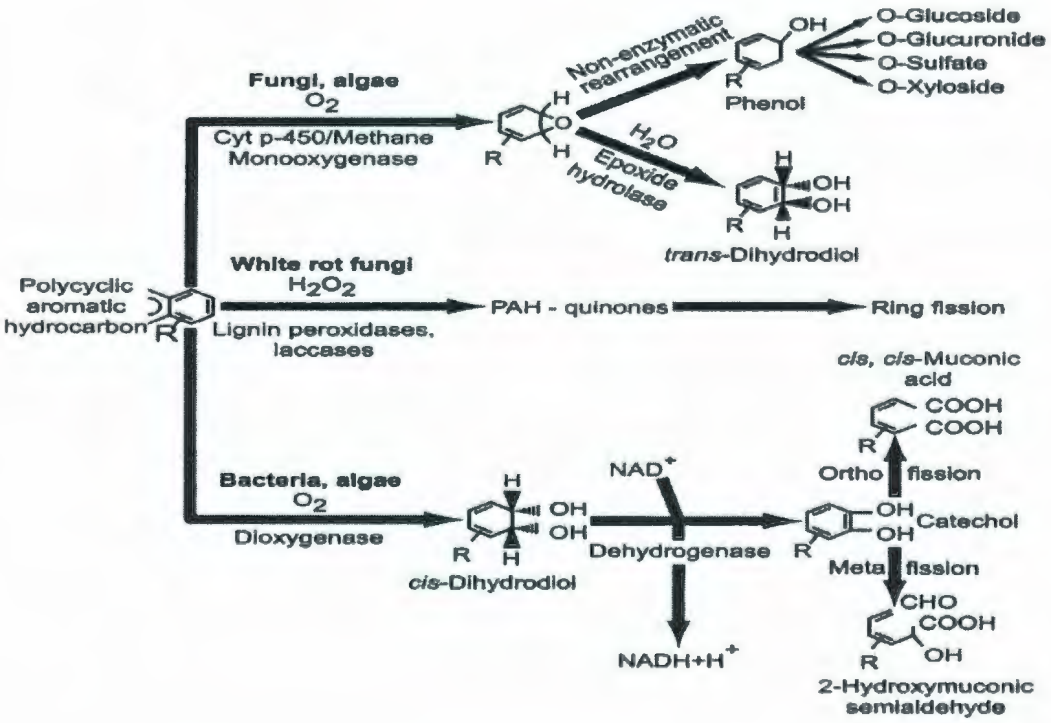


Fig 2.1 Biodegradation of PAHs by prokaryotes (bacteria) and eukariots (fungi, algae, plants, and animals) (Neff, 2002)

2.3 Phenols

Phenol is hydroxybenzene. Phenols, alkylphenols, and some halogenated phenols, are natural components (Buikema et al, 1979). Other phenols could be synthesized by bacteria, fungi, plants, and animals (Neff, 2002).

Concentrations of total phenols in produced water usually range from 0.6 to 23 ppm. The highest concentrations are in produced water samples from the North Sea (Grahl-Nielsen, 1987; Stephenson et al., 1994). Methylphenols (cresols) and dimethyl-phenols (xylenols) are more abundant than phenols in those samples.

Some surfactants are used in the production system to facilitate pumping viscous or waxy crude oils that contain some alkylphenols, may get into the produced water. Table 2.19 shows the concentrations of phenols in produced water in different locations.

Table 2.19: Concentrations of phenols in produced water in different locations (modified from Faksness, 2004).

Compound group	Statfjord B µg/L	Gulfaks C µg/L
C_0-C_3 Phenols	3252	3623
C_4-C_5 Penols	8.63	6.99
C_6-C_9 phenols	1.45	2.03

Solubility of phenols decreases with increasing alkylation. Produced water rarely contains detectable concentrations of the more highly alkylated phenols.

Dougherty (1994) mentioned that phenols do not have a toxic effect on fish and humans but the main concern is that they affect the taste and odor of water. The following table shows some physical properties of phenol.

Table 2.20: Physical properties of phenols (Shiu et al.,1994)

	Aqueous solubility @25°C	Vapour pressure @25°C	Henery's law constant
Phenols	80,000 ppm	53.7 Pa	0.0718 Pa-m^3/mol

The above table indicates that the phenol has a high aqueous solubility but evaporates fast from water. Phenols are rapidly degraded by bacteria and by photolysis (Hwang et al., 1986). However, microbial degradation is faster in the dark than in the light. Phenol at initial concentration in solution of 9,000 µg/L is completely degraded in less than five days in a marine model plankton ecosystem (Kuiper and Hanstveit, 1987).

The biodegradation of the phenol is approximately 1.3 µg/L/hr at a temperature of 17°C to 20°C and an ambient phenol stream concentration of 3 µg/L (Polisions et al., 1975). In less than two hours and at this degradation rate, phenol is completely eliminated from the water. Table 2.21 shows the concentrations of phenol in different locations.

Table 2.21: Concentrations of phenol in different locations.

Locations	Phenols (μg/L)	References
Clean Coastal of China	0.006	Qixing and Limei (1995)
Polluted coastal of China	130	Neff, 2002
Sakhalina Island outer continental shelf, Sea of Japan, The Sea of Okhotsk	<1.0 to 4	(Tkalin, 1993).

2.3.1 Phenols in marine sediments

Due to the partitioning coefficient of phenol, which is very low, log K_{ow} is 1.46 and the log organic carbon/water partition coefficient (log K_{OC}) of about 1.35, phenols are unlikely to accumulate to high concentrations in sediments (Shiu et al., 1994). Other sources of phenols is Los Angeles' treated sewage outfalls in Santa Monica Bay contain an average of 0.018 μg/g phenol (Neff, 2002). Neff et al. (1989b) reported concentrations of phenols in sediments collected 20 m from a produced water discharge in 8 m of water off Louisiana in the range of 0.58 to 3.01 μg/g dry wet.

2.3.2 Bioaccumulation of phenols by marine organism

The bioavailability of phenols depends in part on whether it is in an ionized or un-ionized form in the ambient medium (Westall et al., 1985). The ratio of the ionized to the

unionized form of chemical is correlated with the acidity constant, K_a, also called pK_a. The pK_a is higher than the pH values for a compound. The compound is present in the aqueous phase primarily as the un-ionized. The pK_a for phenol is 9.99 (Lipnick et al., 1985), It is two units higher than the pH of the seawater (8.0), so it means it is un-ionized in the seawater. Demianov et al. (1995) reported that about 94% of phenol is in un-ionized form in the seawater at salinity of 20 to 35%. Thus, other 6% is complexed with sodium, magnesium, and metal cations in the seawater.

Phenol due to its un-ionization form in the seawater, it behaves as a non-polar organic chemical. As confirmed by Davies and Dobbs, 1984; Bierman, 1990, the bioaccumulation of nonpolar organic chemicals by marine organisms is primarily by equilibrium partitioning between the aqueous phase in contact with the organism and the lipids in the organism. The rate of bioaccumulation of phenol from water and the concentration of phenol in the tissues of marine organisms at equilibrium are proportional to the equilibrium distribution coefficient for phenol between the ambient medium and tissue lipids, and this is proportional to the octanol/water partition coefficient (K_{OW}) for phenol (Neff, 2002). Shiu et al., 1994 determined the log K_{OW} for phenol equal 1.46. Bioconcentratable nonpolar organic chemical is defined by EPA as those with log K_{OW} greater than 3.5 (EPA, 1991). This means that phenol is bioavailable and does not bioacumulate to a significant degree in tissues of freshwater and marine organisms. Also, due to active metabolism of phenol in tissues may contribute to its limited bioaccumulation.

The BCFs of 10 and 13 for phenol in Juvenile pink salmon (Oncorhynchus gorbuscha) and kelp shrimp Eualus suckleyi, respectively Saarikoski and Viluksela (1982) developed a regression for 21 phenols.

Log BCF = 1.021 log K_{OW} – 1.82

Where, BCF is bioconcentration factor, K_{OW} is partitioning coefficient, -1.82 is intersect, and 1.021 is slope.

By applying the above equation, it was found that the concentration of phenol in tissues of freshwater and marine organisms should be half of those in the ambient water. Hawker and Connel (1985) reported that bioaccumulation of phenol should be very rapid and the time it takes to reach to equilibrium should be short (a day or less). Korn et al (1985) reported that the fish have a greater ability to metabolize and excrete phenol than the shrimp do. However, by exposing marine prawns, Penaeus japnicus, to phenol concentrations of 5 to 150 µg/L for one year, they accumulate it in their soft tissues to concentrations of 0.09 and 1.82 µg/g dry wet (Qixing, 1999).

Due to the hydeophobicity of the phenol, freshwater and marine organisms bioaccumulate alkyphenols to higher concentrations than phenol (Neff, 2002). Fish have an ability to oxidize phenol and conjugate it with glucuronide and sulfate (Adamson and Sieber, 1974; Kobayashi et al., 1976b; Call et al., 1980). Also, Goldfish excrete unmetabolized phenol and phenyl-β-glucuronide via the gall bladder in the bile and excrete phenylsulfate via the gills (Kobayashi and Akitake, 1975; Kobayashi et al.,1976b). unmetabolized phenol can be excreted passively by fish through the gills. Highest concentrations of total (conjugated and un-conjugated) phenol occur in the bile of exposed fish; lower

concentrations are present in the blood and other body fluids, and lowest concentrations are in organ and muscle tissues (Waluga 1966; Kobayashi et al., 1976a).

2.4 Volume of produced water discharged to the Ocean

The largest volume waste stream in production operations on most offshore platforms is produced water (Stephenson, 1991). The amount of produced water discharged from a single platform is less than 1.5 million L/d and from several platforms could exceed 25 million L/d (Menzie, 1982). In general gas wells produce less amount of produced water than oil wells. The amount of produced water discharged from the Norwegian Sector in the north Sea in 2001 was approximately 116 million m^3 (OLF, 2002). The amount of produced water from the UK offshore facilities reached to 244 million tonnes (Ekins, et al., 2005). The amount of water produced daily in offshore operations worldwide is around 17 million m^3 and about 40% of this amount discharged offshore (OGP, 2005). The volume increases with time, and can, for mature fields, reach over 10 times the volume of the oil produced. Table 2.22 will show the amount of produced water in different locations.

Table 2.22: Amount of produced water from different locations

Location	Amount of produced water L/d	References
U.S Golf of Mexico	> 4,000,000	Neff, 2002
Statfjord	30,000,000	Ynnesdal and Furuholt,1994
West Java Sea	19.100,000 to 97,000,000	Smith et al.,1996
Australia	100,000,000	Neff, 1997a

2.5 Fate and effect of natural constituents in produced water

In order to determine the actual impact of produced water in the marine environment, one needs to consider the fate of the compounds in the environment terms of physical and chemical processes that control their distribution are important as well as the biological interactions of each of the compounds of concern in produced water at the concentrations over the exposure times found in the environment.

2.5.1 Weathering

Weathering is a variety of changes that the compounds contained in produced water face. Dilution, evaporation or volatilization, adsorption/precipitation, biodegradation, and

photoxidation are the most important weathering changes affecting the fate and any subsequent effect of compounds in produced water (OGP, 2005).

These processes as reported by Neff, 1987 tend to reduce the concentrations of compounds in the receiving environment and, thereby, decrease their potential toxicity to marine organisms.

2.5.2 Dilution and dispersion of produced water

Saline produced water dilutes rapidly upon discharge the seawater. Dilution could happen in two phases: an initial or near-field turbulent dilution phase during the first few minutes after discharge, and the subsequent far-field laminar dilution phase that takes place over several hours or days.

The initial dilution in the near-field is defined as the dimensionless ratio of pollutant concentration in the wastewater effluent prior to discharge to the concentration at an equilibrium level, or the free surface, or seabed. Initial dilution occurs because of the entrainment of the surrounding fluid during the rise or sink of the effluent from the outfall ports. Due to the buoyancy resulting from the difference between the densities of produced water and seawater the rising or sinking motion occurs (Davis et al., 1999).

Over the past decade, several studies including field measurements of produced water dilution have been carried out in different parts of the world. Among these are comprehensive, combined measurement and monitoring studies in the Gulf of Mexico, the North Sea and Indonesia. A rapid initial dilution of produced water, even in shallow areas discharged to sea happens (OGP, 2005) within the first few tens of meters of the

discharge point, both field measurements and dispersion modeling studies of the fate of produced water differ in specific details but all predict a rapid initial dilution of discharges by a 30 to 100-fold factor (Neff, 2002).

The dilution rates are slower at the far field. At distances from 500-1000 meters away from the discharge point, dilution rate of 1000-100,000-fold normally occurs(OGP, 2005).

Once discharged, the produced water plume will descend or ascend depending on its relative density to the ambient seawater, and it will bend in the direction of the ambient current until it encounters the seafloor or reaches the water surface. The near-field phase in which the plume usually be trapped at a neutrally buoyant level before it encounters the seafloor or reaches the water surface, this phase ends within minutes and within a few meters from the discharge source and the corresponding dilution is in the range of 100 to 1,000.

After the plume reaches the boundary (surface/seabed), it spreads as a thin layer and the mixing is dominated by two mechanisms: buoyant spreading and oceanic turbulent diffusion. Due to the residual buoyancy contained in the plume, buoyant spreading is a self-driven dispersion process because the horizontal transverse spreading and vertical collapse of the plume. Because of the oceanic turbulence or eddies, turbulent diffusion is a passive dispersion process. Both buoyant spreading and turbulent diffusion are important over a distance from the discharge point but the buoyancy effect decreases while the turbulence effect increases as a plume travels downstream.

Produced water salinities are likely to change rapidly toward that of the ambient seawater following discharge. Smith et. al. (1994) reported that the produced water being

discharged through a 15 cm diameter pipe at rates of 460,000 L/day to 1.03 million L/day in a water depth of 82 m was diluted 100-fold within 103 m of the discharge. The ambient current speeds ranged from 0.05 to 0.28 m/s.

Following discharge, phenols and alkylphenols are diluted rapidly. Phenol is not persistent in marine and freshwater. phenol goes into aqueous solution readily but evaporates from water and is also rapidly degraded by resident bacteria and by photolysis. Many factors affect removing of phenol from water column rapidly upon discharge as the combined dilution, microbio- and photo-degradation, and evaporation (Neff, 2002).

Also, PAHs in produced water dilute rapidly upon discharge. Exposing PAHs to solar radiation several reactions undergo and produce a variety of mostly or more polar organic compounds. While many of photo-oxidation products dissolve in the water column, some high molecular weight compounds that are soluble in either water or oil maybe produced. Increasing water depth decreases the rate of photolysis of PAHs because of the ultraviolet light intensity decreases logarithmically with depth in the ocean.

2.5.3 Dilution Models

Different models of dilutions are now available as CORMIX (Doneker & Jirka, 1990), PLUMES/VISUAL PLUMES (Baumgartner et al, 1994), OMZA (Huang & Fergen, 1996), TRK (Riddle, 1993), VISJET (Lee &Chu, 2003), DREAM (Johsen et al., 1999) and BJET (Nilsson, 1991).

CORMIX (Cornell Mixing Zone Expert System Model; Doneker and Jirka, 1990) is the USEPA surface water transport model. CORMIX forces a submerged single port discharge to be in the bottom 1/3 of the water column. Produced water discharges normally discharged on or close to the surface.

OMZA was developed by Huang & Fergen (1996). To predict behaviors, OMZA uses a three-rank jet classification concept and an all-regime prediction method, for the near field buoyant jet mixing process. To predict the far field dilution for the far field plume mixing process, OMZA uses a model that includes both buoyant spreading and turbulent diffusion. OMZA model neglects the wave effect.

DREAM (the Dose Response Effects Assessment Model), is developed by Johnsen et al. (1999), predicts the effects to fish and zooplankton to complex mixtures of chemicals. DREAM is a deterministic approach. Due to natural variability of reservoirs and differences in the process equipment used in separating the contaminants from produced water, the types and quantities of chemicals in produced water are variable.

VISJET (Lee and Chu) is a general interactive computer modeling system that predicts the impact of an effluent discharge into the water environment. This model is based on the Lagragian model JETLAG. The model only describes the near field mixing and the wave effect is neglicted.

CHARM model is developed by Aquateam-Norwegian Water Technology Centre A/S (N) and TNO- Marine Laboratory (NL), (Schobben et al., 1994; Ofjord et al., 1995). The model enables a stepwise environmental evaluation by means of a successive pre-screening, Hazard Assessment, Risk Analysis, and Risk Management on the basis of available data on the chemicals and platform related conditions.

2.5.4 Some ambient considerations used in the dilution models

Ambient conditions cannot be neglected, which they play an important role in the concentrations of pollutants that enter the mixing zone. These include receiving water depth, current, density stratification, tidal fluctuations, channel configuration, and bottom geometry. This part will not discuss in details because it is out of the scope of the research.

In general, the deeper the discharge, the better chance there is meeting regulations. According to that reason, it is important to change the regulation of discharging produced water, which is used to discharge close to the surface. More deeper means more water is available for dilution, so there is less chance of impingement with the bottom and surface and the trajectory of the plume become longer before reaching the surface. Discharge into shallow water is always a problem. The plume quickly fills the water column. The rate of dilution decreases, when the plume hits the bottom or surface of the receiving water (Davis, L.R.,1999).

Ambient density stratification can have an important effect on plume dynamics. As the jet mixes with the ambient, the plume's density increases gradually till approaching that of the ambient (Davis, L.R, 1999).

The ambient current affects the plume in a variety of ways. The ambient current always carries the plume in the direction of the current regardless of the direction of the discharge (Davis, LR, 1999).

Tides cause both the depth, current, and current direction to vary with time. In addition, since most tidal concerns are in coastal areas. Mixing zone models are unable to predict tidal conditions, because they depend on steady state conditions (Davis, LR, 1999).

According to the above mentioned, we can find that the CHARM model can be applied in this study to calculate the dilution of produced water. In CHARM model the dilution factor is assumed to be 1:1000 at a distance of 500 m from the release site in the hazard assessment mode. This factor is predicted by experimental work and it is similar with the calculated one by CHARM model.

The dilution model as used in the CHARM risk assessment model is:

Dilution = $C_o/C = ULH/Q_O = V/ Q_O (96K_Z X^3/U)^{1/2}$

Where,

C_o = concentration of tracer in the outlet opening (g/m^3)

C = concentration of tracer measured in the recipient (g/m^3)

U = average current velocity (m^3/s)

L = Width of the plume diluted in the seawater (m)

H = depth (m)

Q_O = the release rate through the outlet opening (m^3/s)

V = horizontal diffusion velocity (m/s)

K_Z = vertical diffusion coefficient (m^2/s)

X = distance from the source (m)

The parameter V expresses the lateral spread of the release (the sidespread). The parameter K_Z expresses the ability for the ambient water of vertical mixing.

2.5.5 Volatilization of compounds of produced water

After discharge, the low molecular weight fractions of the organic components in produced water will either volatilize into the air or will be degraded by either photolytic or biological processes. Low molecular weight aliphatic and aromatic hydrocarbons tend to evaporate rapidly from the produced water mixtures.

2.5.6 Adsorption and sedimentation of produced water

Despite of different physiochemical reasons, both the inorganic and organic constituents in produced water tend to adsorb on suspended solids present in both produced water and seawater. Two factors are controlled this process: the amount of suspended solids and the adsorption behavior of the individual constituents. With increasing molecular weight, the adsorptive tendency of carboxylates towards clays increases. Adsorbed oil tends to stabilize the suspended solids, slowing their sedimentations (OGP, 2005).

2.5.7 Biodegradation of produced water

the major decomposition pathway for organic compounds in the aquatic environment is biodegradation. Biodegradation occurs both in water column and in sediments. Whereas aerobic processes dominate degradation, biodegradation in water column, biodegradation in sediments can proceed by either aerobic or anaerobic processes (OGP, 2005). The susceptibility of compounds to biodegradation is determined by their chemical structure. Around 50% of biomass of seawater is unicellular organisms, and these organisms

dominate active biological surfaces in seawater (Melbyed and Brakstad, 2001). Biodegradation is very important because it is responsible of the overall removal of organic compounds in produced water plumes, and also, it depends primarily on the presence of the majority of the organic compounds and the selection of bacteria in the local microbial community that are able to degrade specific organic compounds in produced water.

Chapter 3

Experimental Work (partitioning of produced water) and Results and Discussion

3.1 Objective

The objective of the experimental work is to identify the amount of PAHs and phenols in the water phase in produced water after partitioning in the water phase.

This experiment is not to verify or repeat Faksness' experiment (faksness et al., 2004) but to apply risk assessment tools to study the effects of PAHs and phenols after partitioning in the water phase on marine organisms and in humans. This chapter describes the apparatus used and steps involved in conducting the experiments.

3.2 Previous Work

The partitioning of produced water has been done by Faksness et al (2004). Faksness studied the partitioning of semi-soluble components of produced water, such as PAHs and phenols. His results were promising and gave an idea about how produced water components behave. Faksness' results showed that there is a correlation between the concentration of dispersed oil in the produced water and the concentration of semi-soluble aromatic hydrocarbons and alkylated phenols.

3.3 Experimental work

The produced water experiments were performed at Memorial University laboratory. One closed bottle (20 L) with a drain valve for sampling was used. The experimental setup is shown in the following figure.

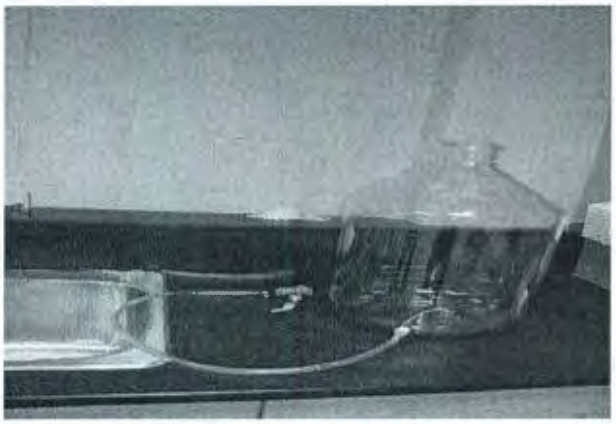


Fig.3.1 experimental work setup

3.4 Procedure

Produced waters were obtained after treatment from the Hibernia offshore platform. The dispersed oil in produced waters was less than 40ppm (mg/L). The experiments were carried out twice on two different batches of produced waters. The first produced water was collected by the DFO (Department of Fisheries and Oceans) in Newfoundland in July, 2007 from the Hibernia offshore platform and preserved in temperature less than 4°C for one year. The second batch was also collected by DFO in Newfoundland and Labrador in July, 2008 from Terra Nova offshore platform. Table 3.1 shows the concentrations of PAHs in the two batches of produced water.

Table 3.1: The concentration of PAHs and phenols before partitioning in old and new batch of produced water (Hibernia, 2007 and Terra Nova, 2008)

	Compounds	Concentrations in July 2007 (µg/L)	Concentrations of old pw after 1 year (µg/L)	Concentrations of PAHs new pw (µg/L)
Naphthalene	Naphthalene	113.7	6.6	19
	C1-naphthalene	79.8	3.1	7
	C2-Naphthalene	NR	1.9	4.1
2-3 rings PAHS	Acenaphthene	1.1	0.06	ND
	Acenaphthylene	NR	0.03	ND
	Fluorene	6.3	0.28	0.2
	Phenanthrene	11.1	0.37	0.2
	Anthracene	ND	ND	ND
	Pyrene	0.35	0.02	ND
4-6 rings PAHs	Fluoranthene	0.14	0.01	ND
	Chrysene	1.5	ND	ND
	Benzo(b)fluoranthene	0.22	ND	0.1
	Benz(a)anthracene	0.16	0.06	ND
	Benzo(k)fluoranthene	NR	0.01	0.1
	Benzo(a)pyrene	0.13	0.01	ND
	Benzo(g,h,i)perylene	0.1	0.02	ND
	Perylene	NR	0.04	ND
	Dibenz(a,h)anthracene	0.09	0.01	0.1
	Indeno(1,2,3-	ND	ND	ND
Phenols	Phenol	1219.49	9	6.6

NR: not reported

ND: not determined

From the above table, the concentrations of PAHs and phenols in the produced water collected from the Hibernia offshore platform are much higher than the ones from the Terra Nova offshore platform maybe because of different production techniques used in the two platforms or maybe due to different separation technique. Also, it can be observed that concentrations of the old produced water after one year of storing in a temperature, at 4°C have completely changed when compared to those of the previous analysis. The significant change is low molecular weight PAHs as naphthalene and 2-3 rings PAHs. For the high molecular weight PAHs, such as 4-6 rings PAHs, the changes in concentrations are not significant. The main factor responsible for those changes in the concentrations is degradation.

Two types of degradation occurred during the storing of the produced water for one year:

- Photooxidation of PAHs

This produced water exposed to some light because it is not preserved in a dark place. In general, the rate of photooxidation of aromatic hydrocarbons is 0.004 percent/day (Berthou and Vignier, 1986). It was observed that there were some particles in the produced water precipitated in the bottom of the glassware. Maybe these compounds were the polymerization of PAHs which occurred due to the photooxidation.

- Microbial degradation

From the literature review, it can be seen that the microbial degradation for naphthalene ranges from nondeductible to 19.8 $mg/m^3/day$ (Massie et al, 1985), so in this case, we will assume that there was a significant effect of microbial degradation on naphthalene, but that it was not in at a high rate. High molecular weight PAHs can be completely

degraded after nine months, as reported by Fayad and Overton (1995). In this case, a complete degradation of Chrysene, Benzo(b)fluoranthene, and Indeno(1,2,3-cd)pyrene occurred.

The samples were taken from the bottom of the bottle, every 12 hours time (t) intervals = 0, 12, 24, 36, 48 hrs. The samples for PAHs were taken in 250 mL glass bottle and 100 mL amber glass bottle preserved with sulphuric acid for total phenols pH<2.

The analysis for PAHs and phenols was done by Maxxim Analytics Inc. in St. John's, NL, Canada. GC-MS (Gas chromatography/ mass spectrometry) was used for the analysis. EPA 8270C and EPA 420.2 methods were used to determine the concentration of PAHs and phenols respectively. The following figure shows the steps of partitioning of produced water

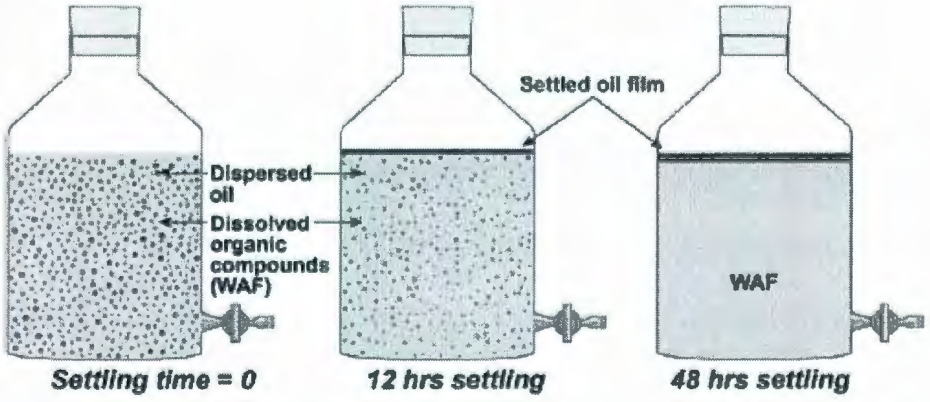


Fig. 3.2 Steps of partitioning of produced water (Faksness, 2004)

3.4.1 The old batch of produced water (Hibernia, 2007)

The following figure shows the steps of partitioning of the old patch of produced water.

Fig. 3.3: Old batch of produced water before partitioning, after 24 hours, after 36 hours, and after 48 hours respectively and also shows the oil phase inside the glassware as dark rings

From the above figure, we can see the precipitating of the oil phase in the glassware's wall. And also, after one day of partitioning, it was observed that the turbidity of produced water and the yellow color were gone and the water became more clear.

3.4.2 The new batch of produced water (Terra Nova, 2008)

The same procedure was followed in the partitioning of the new batch of produced water from the Terra Nova offshore platform after treatment. The oil content in this produced

water was less than 40ppm. The following figure (Fig. 3.5) shows the partitioning steps of produced water every 12 hours.

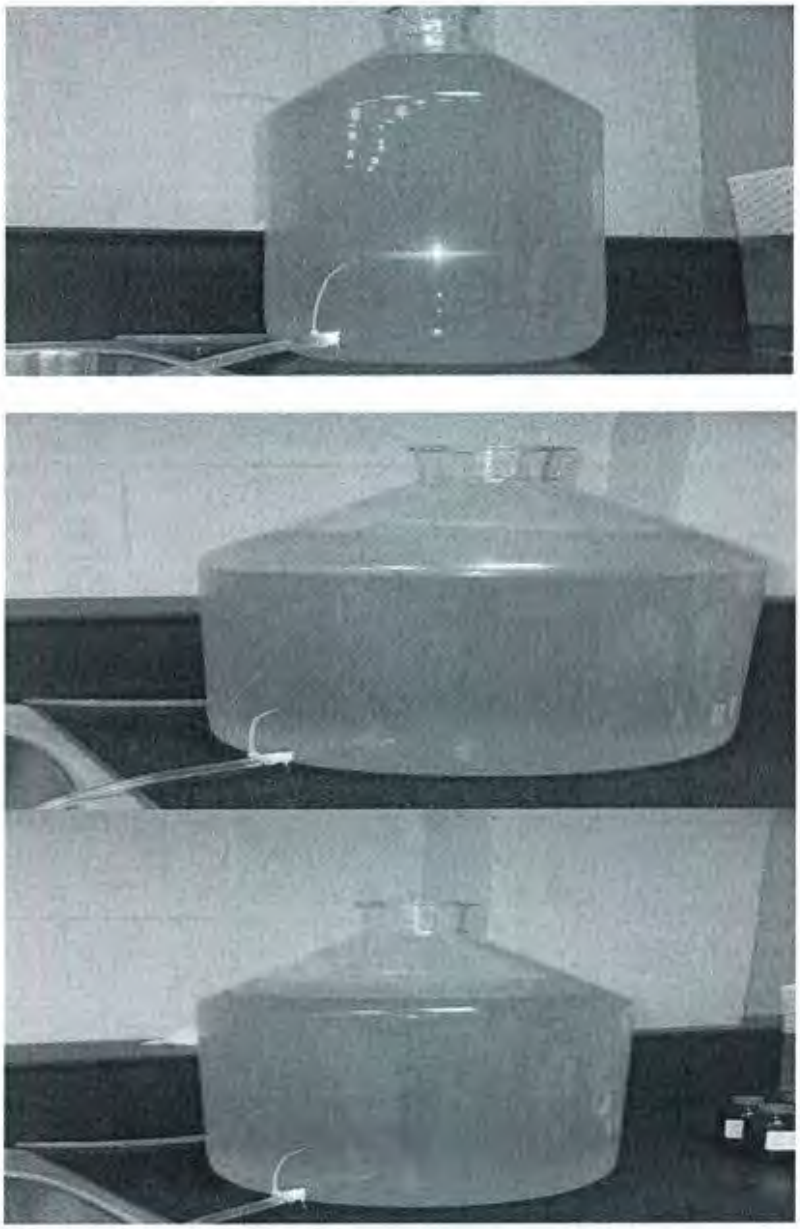


Fig.3.4. The partitioning of the new batch of produced water before partitioning, after 12 hours, after 24 hours, after 36 hours, after 48 hours and after 60 hours respectively

From Fig.3.4, it can be seen that the oil phase was observed inside the glassware's wall but its color was not brown as in the old batch of produced water, which was preserved for around a year. The brown color have occurred because of oxidation that could happen

to some components of produced water or maybe because of transformation of some components to some complex compounds.

3.5 Results and Discussion

3.5.1. Introduction

This chapter discusses the results from the partitioning of two different batches of produced water which were collected by department of Fisheries and Oceans of Canada (DFO) in Newfoundland from the Hibernia offshore platform in 2007 and the Terra Nova offshore platform, 2008.

3.6 Results of partitioning of produced water

The first batch of produced water was collected by DFO from the Hibernia offshore platform in July, 2007. The concentration of PAHs before and after partitioning is presented in Table 3.2.

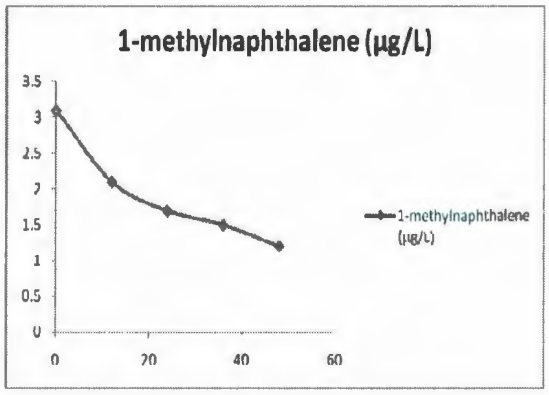
3.6.1 Results of partitioning of old batch of produced water (Hibernia, 2007)

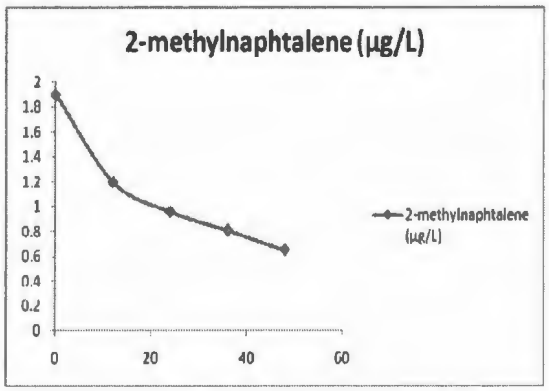
Table 3.2 Concentrations of PAHs in the old batch of produced water (Hibernia, July 2007) before and after partitioning:

	PAHs	Concentrations of PAHs before partitioning (μg/L)	Concentrations of PAHs after partitioning (μg/L)
Naphthalene	Naphthalene	6.6	2.8
	C_1-naphthalene	3.1	1.2
	C_2-naphthalene	1.9	0.65
2-3 rings PAHS	Acenaphthene	0.06	0.02
	Acenaphthylene	0.03	ND
	Fluorene	0.28	0.08
	Phenanthrene	0.37	0.09
	Anthracene	ND	ND
	Pyrene	0.02	ND
4-6 rings PAHs	Fluoranthene	0.01	ND
	Chrysene	ND	ND
	Benzo(b)fluoranthene	ND	ND
	Benz(a)anthracene	0.06	ND
	Benzo(k)fluoranthene	0.01	ND
	Benzo(a)pyrene	0.01	ND
	Benzo(g,h,i)perylene	0.02	ND
	Perylene	0.04	ND
	Dibenz(a,h)anthracene	0.01	ND
	Indeno(1,2,3-	ND	ND

From the above table, it can be seen that most of the high molecular weight PAHs, such as 4-6 rings PAHs, disappeared from the water phase, and this is because the high molecular weight PAHs have K_{ow} >4, so they tend to partition in the oil phase, not in the water phase. Other PAHs with low molecular weights, such as naphthalene tend to remain in the water phase because they have K_{ow}<4. The concentration of naphthalene decreases after partitioning from 6.6 to 2.8 μg/L, may be due to partitioning of naphthalene into the air.

The results of partitioning of old produced water show there is no difference in the concentration of PAHs in produced water before and after partitioning. The change of concentrations of naphthalene and 2-3 rings PAHs and 4-6 rings PAHs are represented in the following figures.





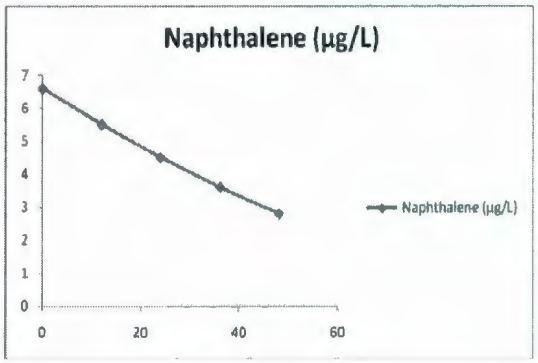
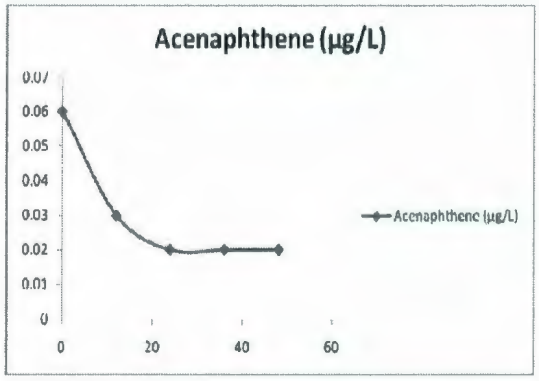
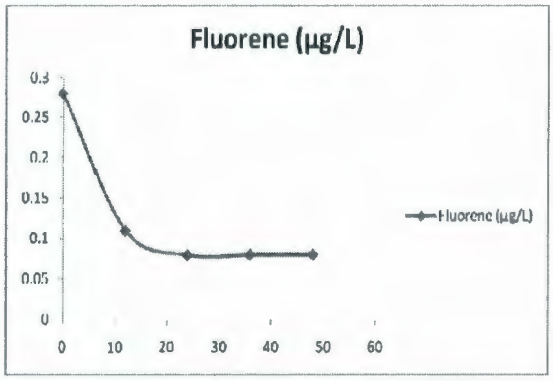


Fig. 3.5 Concentrations of Naphthalene in the old batch of produced water during partitioning for 5 samples every 12 hours in the water phase

Fig. 3.5 shows the partitioning of naphthalene in times of 0, 12, 24, 36, and 48 hours, starting with a concentration 6.6 µg/L until reaching equilibrium after 48 hours, at 2.8 µg/L. From these graphs, we find that there is a relation between dispersed oil in produced water and concentrations of naphthalene. This means when the amount of dispersed oil decreases the concentration of naphthalene also decreases.

The change of concentrations of 2-3 rings PAHs is represented in Fig. 3.6





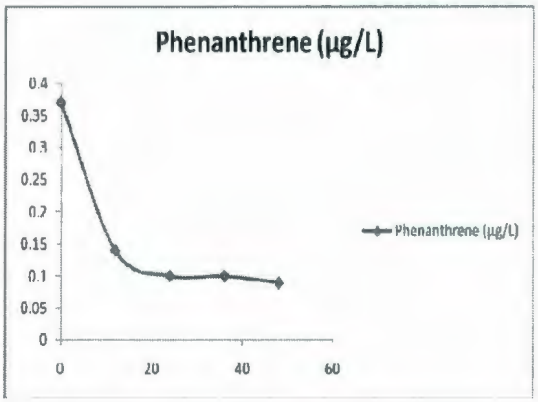


Fig 3.6: Concentrations of 2-3 rings PAHs in the old batch of produced water during partitioning for 5 samples every 12 hours in the water phase

From Fig. 3.6, we see that there is a relation between the amount of dispersed oil and concentrations of 2-3 rings PAHs. When the amount of oil reduces in the water phase the concentrations of 2-3 rings PAHs decrease. This is because they have log $K_{ow} \geq 4$, so their tendency to remain in the oil phase rather than in the water phase increases. An example acenaphthylene, which disappeared from the water phase. However, fluorene and phenanthrene have log $K_{ow} > 4$ and greater than log K_{ow} of acenaphthylene (4.18, 4.12, 3.92 respectively) but they are still in the water phase, but in very small concentrations. This could be explained due to the fact that acenaphthylene was in a very small concentration, so that any change in concentration will be very difficult to detect. For fluorene and phenanthrene their concentrations decrease from 0.28 and 0.37 6 µg/L respectively to 0.08 and 0.09 6 µg/L respectively and these concentrations fall within the detection limit of GC-MS.

Fig 3.7 shows the change of concentrations of 4-6 rings PAHs in the old batch of produced water.

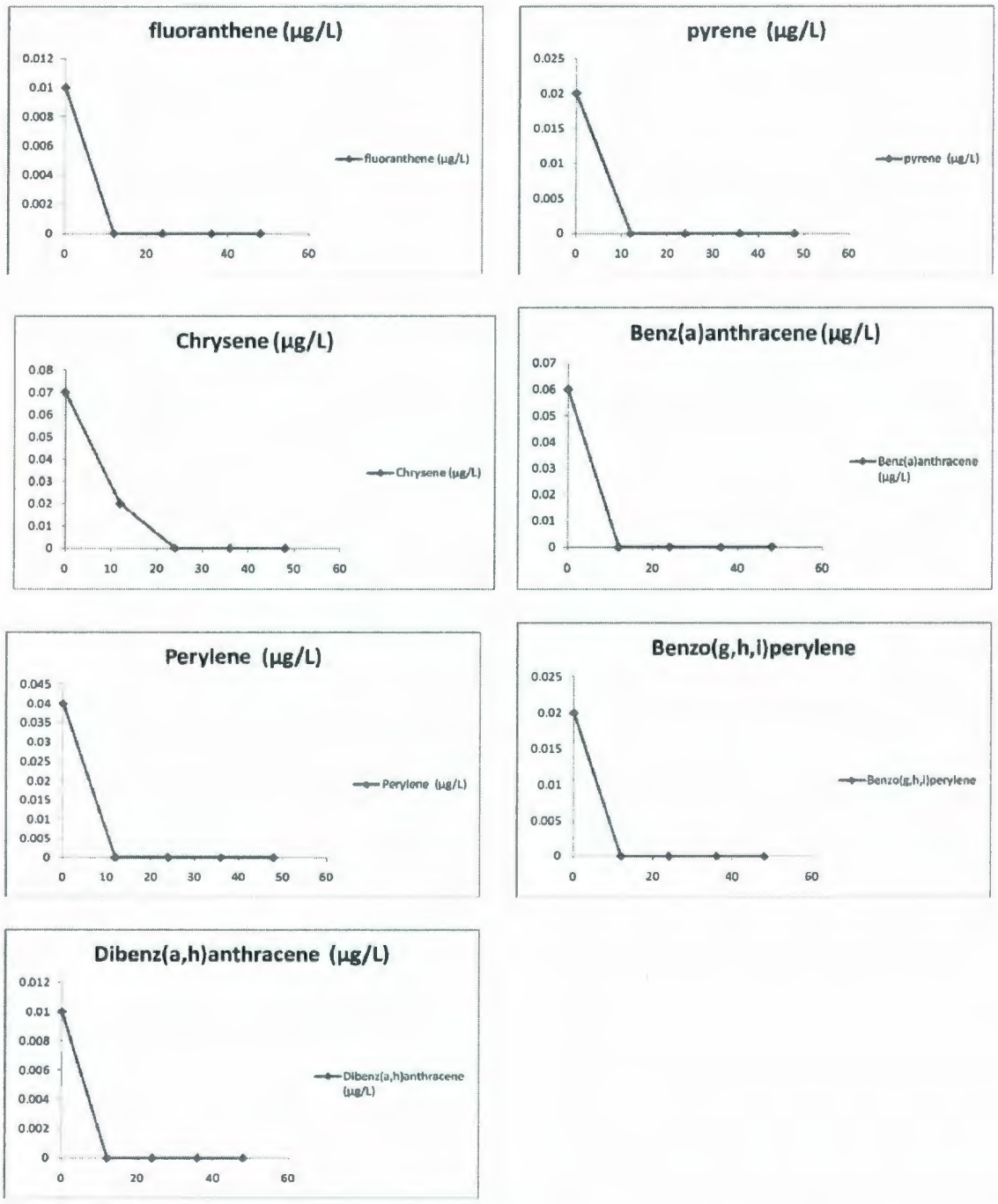


Fig. 3.7 Concentrations of 4-6 rings PAHs in the old batch of produced water during partitioning for 5 samples every 12 hours in the water phase

From Fig 3.7, it can be determined that all 4-6 rings PAHs disappeared from the water phase, and this is normal because they have a log $K_{ow} > 4$.

From the partition experiment on the old produced water, it was found that the change in concentrations of 2-3 rings and 4-6 rings PAHs are so small. That it is hard to assume that there is a relation between the amount of dispersed oil in the water and concentrations of 2-3 rings and 4-6 rings PAHs.

3.6.2 Results of partitioning of the new batch of produced water (Terra Nova, 2008)

The analysis of the new patch of produced water, which was also collected by DFO from the Terra Nova offshore platform, in Aug, 2008, is presented in Table 3.3.

Table 3.3 Concentrations of PAHs in the new batch produced water (Terra Nova, Aug. 2008) before and after partitioning:

	PAHs	Concentrations of PAHs before partitioning (μg/L)	Concentrations of PAHs after partitioning (μg/L)
Naphthalene	Naphthalene	19	12
	C1-naphthalene	7	4.3
	C2-naphthalene	4.1	2.5
2-3 rings PAHs	Acenaphthene	ND	ND
	Acenaphthylene	ND	ND
	Fluorene	0.2	ND

	Phenanthrene	0.2	0.2
	Anthracene	ND	ND
4-6 rings PAHs	Pyrene	ND	ND
	Fluoranthene	ND	ND
	Chrysene	ND	ND
	Benzo(b)fluoranthene	0.1	ND
	Benz(a)anthracene	ND	ND
	Benzo(k)fluoranthene	0.1	ND
	Benzo(a)pyrene	ND	ND
	Benzo(g,h,i)perylene	ND	ND
	Perylene	ND	ND
	Dibenz(a,h)anthracene	0.1	ND
	Indeno(1,2,3-	ND	ND

The above table shows that there is a change in the concentrations of PAHs before and after partitioning. All changes in the concentrations of PAHs in the new batch of produced water consistent with the disscusion of the results of partitioning of the old batch of produced water The following figure shows the change of concentrations of naphthalenes during partitioning.

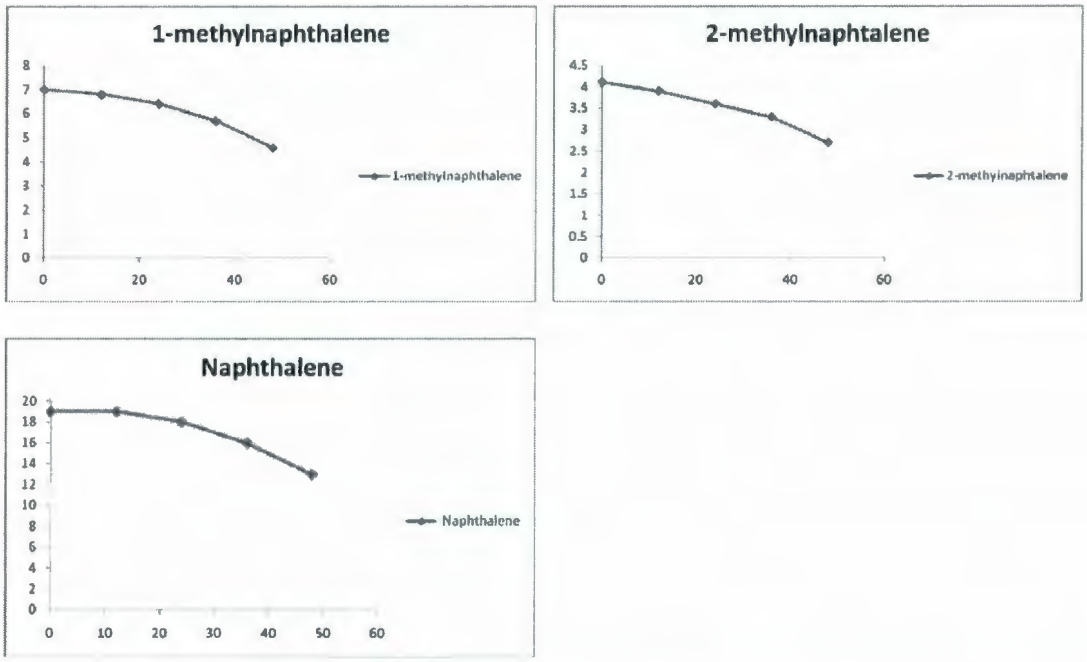


Fig. 3.8 Concentrations of naphthalenes in the new batch of produced water during partitioning for 5 samples every 12 hours in the water phase

Fig. 3.8 confirms that there is a releation between the amount of dispersed oil in the water and concentrations of naphthalenes.

Fig 3.9 shows the partitioning of 2-3 rings PAHs.

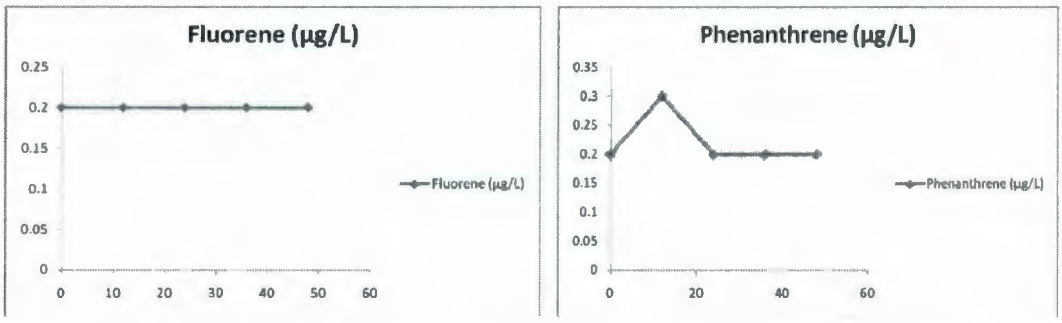


Fig. 3.9 Concentrations of 2-3 rings PAHs in the new batch of produced water during partitioning for 5 samples every 12 hours in the water phase

As revealed in Fig. 3.9 there is no relation between the amount of dispersed oil in the water and concentrations of 2-3 rings PAHs. In the old produced water there was a slight change in the concentration. This change was due to the accuracy in analysis which has some errors around 1%. The following figure shows the partitioning of 4-6 rings PAHs.

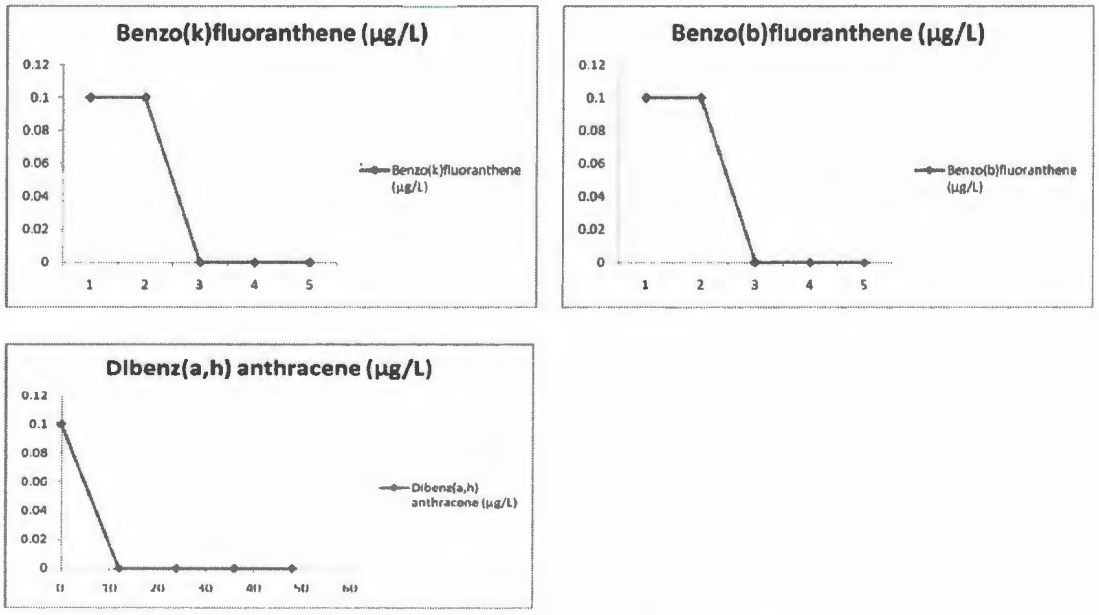


Fig. 3.10 Concentrations of 4-6 rings PAHs in the new batch of produced water during partitioning for 5 samples every 12 hours in the water phase

Fig.3.10 confirms the relation between the amount of dispersed oil in the water and concentrations of 4-6 rings PAHs.

Regarding the experimental work, the most abundant PAHs in produced water are the more water-soluble 2-3 rings (Naphthalene, phenanthrene and fluorene) and their alkylated homologues. High molecular weight PAHs, such as the carcinogen PAH,

benzo(a)pyrene, are almost never present at greater than ultratrace (<1 μg/L) (Neff and Saur, 1996), and this is confirmed in these experiments, when most of the high molecular weight PAHs present in <0.1 μg/L.

According to Thomann (1989), as a general rule, nonpolar organic hydrocarbons, including PAHs with log partitioning coefficients (Log K_{OW}) less than 5, tend to partition into or onto all hydrophobic surfaces.

All PAHs, with the exception of naphthalene, have Log K_{OW}s greater than 3.5 (Mackay et al., 1992) and, therefore, have a strong tendency to bioaccumulate in tissues of marine organisms (Neff and Saur, 1996).

3.6.3 Analysis of phenols

The partitioning of phenols in the Terra Nova offshore platform is shown in the following figure.

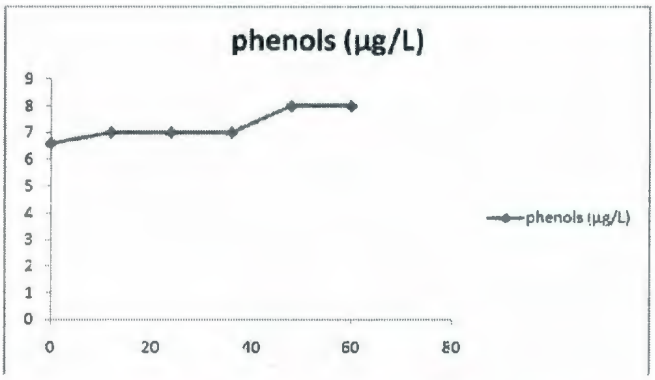


Fig 3.11. Concentrations of phenols in the new batch of produced water during partitioning for 6 samples every 12 hours in the water phase

According to the diagram, we find that the concentration of phenols increased in the water phase from 6.6 to 8 µg/L after 48 hours. This means that some phenols in the oil phase started to dissolve into the water phase. According to Neff (2002), phenols reach equilibrium in fish lipid tissue after 2 or 3 hours, which means that partitioning here depends on the type of exposed surface (for example water, air, lipid, sediments, etc.).

Table 3.3 shows the difference in concentrations of the same produced water in 2007 and after one year.

Chapter 4

Ecological risk assessment and human risk assessment

4.1 Introduction

Ecological risk assessment is defined by USEPA (1998) as" a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors". Ecological risk assessment is a process to analyze data and uncertainty, to evaluate the likelihood of adverse effects on the marine environment (Anderson et al, 1997). Three distinct phases of ecological risk assessment are used in this study: problem formulation, analysis, and risk characterization.

The purpose of ecological risk assessment is to contribute to the protection and management of the environment through scientifically credible evaluation of the ecological effects of human activities (Suter and Barnthouse, 1992). It is difficult to define the objectives and specific procedures for ecological risk assessment because there are others pollutants in the environment not only the presence of produced water.

In this chapter, the methodologies of the ecological risk associated with PAHs and phenols in produced water discharges from offshore operations will be discussed.

4.2 Ecological risk from contaminants in produced water

In the last two decades, the ecological risk assessment of produced water has gained much attention. To assess the ecological risk from produced water, numerous studies on ERA have been carried out (Brendehaug et al., 1992; Stagg et al, 1996; Neff, 1979; Neff and Sauer, 1996; Neff et al., 1997; Neff, 2002; Booman and Foyn, 1996).

A quantitave ERA was performed to evaluate risks associated with produced water discharged from Statfjord and Gulfaks fields (Karman et al., 1996). A quantitave ERA is an approach based on the Chemical Hazard Assessment and Risk Management (CHARM, Thatcher et al., 1999) model, was employed in the Karmen et al.(1996) study. The CHARM model was originally developed for ERA of discharges related to offshore oil operations in the North Sea. In this model, the ecological risk is calculated by taking the ratio of predicted environmental concentration to predict no-effect concentration (PEC/PNEC). For calculating PNEC in water, the NOEC (No Observed Effect Concentration) for the most sensitive effect parameter (e.g., growth, reproduction) is considered when data is available.

When toxicity data for several species is available, PNEC is defined as (Karman et al., 1996) :

$$PNEC = \frac{GM}{1000\sqrt{n}}$$

Where GM is the geometric mean of available EC_{50} values (i.e. chemical concentration resulting in observed effects in 50% of test animals), n is the number of species for which

toxicity data is available for a particular chemical. The coefficient of 1000 is a subjective factor (French, 1999).

Karman and Reenik (1998) proposed a dynamic assessment of the ecological risk by assuming the risks can be estimated from the ratio of time-integrated predicted environmental concentration (PEC) to time-adjusted predicted no-effect concentration (PNEC).

In 2007 a new approach was used to assess risk from PW, which called POM–RW. POM-RW (the Princeton Ocean Model and a Random Walk) is a numerical approach developed by Chen et al. (2007), which based on an integration of the Princeton Ocean Model and a Random Walk simulation of pollutant transport. This model was build to simulate the ocean current, also provide a three dimensional hydrodynamic input to a random walk model focused on the dispersion of toxic components within the produced water stream. The validation of the model was done and indicated that is a useful approach to assess risks of produced water. Reed (1996) suggested that the focus of future research in environmental risk of produced water should be on potential chronic effects. Reed et al. (1996) presented a model called PROVANN for assessing potential chronic effects of produced water. The model consists of four components: a near-field release model, a far-field transport model, a biological exposure model, and a bioaccumulation and biomagnifications model. PROVANN was modified into DREAM (Dose Related Risk and Effects Assessment Model) (Reed, 1999). DREAM addresses several problems in ERA, including time-space variations of discharge concentration fields, exposure of

organisms with different behavior patterns, assessment of mixture of chemicals, and assessment of sub-lethal chronic effects in terms of body burdens.

4.3 Toxicity of whole produced water

Produced waters from oil and gas wells vary widely in chemical compositions and toxicity to freshwater and marine organisms. Caliani, et al. (2009) reported that the produced water has a genotoxic effects on fish, it was found that there is a DNA damage happened after exposing for 30 days with pw concentration 10%. Also, Holth et al (2008) found there is a chronic effect of environmentally relevant concentrations of PW on ziberafish, in which its gene expression and population are affected negatively. Hylland et al.(2008) reported that there is a minor environmental impact in the water column around the offshore platforms in the North Sea and cause a low effect on the cod fish. Fucik (1992) reported that some low salinity produced waters are used in arid regions of Wyoming, USA, as a water source for livestock. Other produced waters are saturated brines (about 300% salinity) containing high concentrations of organic acids, hydrocarbons, phenols, metals, and radionuclides. The toxicity of produced waters is related to their chemical compositions, and varying widely from nontoxic (LC_{50}>100 percent effluent) to moderately toxic (LC_{50}<1 percent) (Neff, 2002).

In estimating the risk of produced water discharges to marine organisms and ecosystems in the receiving water environment, one can compare the estimated or measured dilution of the produced water plume in the receiving water at different distances from the discharge point to produced water concentrations known to cause adverse effects in

marine organisms. The causative agents of toxicity of produced waters is not known, but may be related to the extremely high total dissolved solids (salinity) concentrations, altered ratios of major seawater ions, and elevated concentrations of ammonia in some Gulf of Mexico produced waters (Moffitt et al., 1992).

There are poorly characterized species differences in the toxicity of produced waters to marine organisms (Neff, 2002). Where bioassays are done with two or more marine taxa and the same sample of produced water, crustaceans usually are more sensitive than fish (Neff, 1987; Louisiana Department of Environmental Conservation, 1990; Jacobs and Marquenie, 1991;Terrens and Tait, 1993).

Table 4.1: Summary of the acute, sublethal, and chronic toxicity of produced waters throughout the world to different taxa of marine and freshwater organisms. Effects concentrations in produced water (Stephenson et al.,1994)

Taxon	Species	Endpoint	Duration (days)	EC50/LC50
Algae	Phaeodactylum tricorntum	Growth	4	0.09-3.6
	Skeletonema costatum	Growth	2	4.5-67.6
Coelenterates	Campanularia flexuosa	Growth	10	5.0
Bivalve Mollusks	Crassostrea gigas larvae	Mortality	2	5.0
	Mytilus californianus larvae	Shell	2	2.1
	Donax faba adults	Mortality	4	0.02-15.3
Polychaetes	Neanthes arenaceodentata	Mortality	4	18.1-28.6
Copepods	Tisbe holothuriae	Mortality	4	35.7-66.7
	Calanus Finmarchicus	Mortality	1	10

	Acartia tonsa	Mortality	2	2-18
		Reproduction	20	0.3-5.0
		Immobility	4	2.0
Amphipods	Alorchestia compressa	Mortality	4	29.4->100
	Chaetogammarus	Mortality	4	0.2-3.2
Shrimp	Penaeus aztecus Larvae	Mortality	2	0.8-1.2
	Penaeus aztecus Juveniles	Mortality	4	6-18.3
	Penaeus aztecus adults	Mortality	4	7.8-17.8
	Penaeus stiferus adults	Mortality	4	7
	Crangon crangon adults	Mortality	1	2
Brine shrimp	Artemia salina	Mortality	1	16-18
Mysids	Americamysis bahia	Mortality	4	4.9-11.8
		Mortality	7	4.4-9
		Fecundity	7	0.7-7
Barnacles	Balanus tintinabulum	Mortality	4	8.3
Fish	Menidia beryllina larvae	Mortality	4	>1.1-5.5
	Hypleurochilus germinatus	Mortality	4	15.8-40.8
	Cyprino variegatus	Mortality	4	7.2-60
		Mortality	7	3.7->28
	Poecilia reticulata	Mortality	4	0.75-42.3
		Mortality	2	10.0

Median effects concentration (EC_{50}) or median lethal concentration (LC_{50})

From the above table, it can be seen that the acute and sublethal effects concentrations as (EC_{50} or LC_{50}) of whole produced water ranged from 0.02 to more than 100 percent. In general, marine algae, bivalve mollusk larvae, and various species of crustaceans, particularly larval forms are the most sensitive marine organisms. Generally, fish are more tolerant to produced water than marine invertebrates. Reproductive success in

Acartia and fecundity in Americamysis, are more sensitive indicators of toxic effects than acute mortality (Neff, 2002).

The 5% to 10% concentration of typical produced water from the North Sea platform shows 50% reduction in growth (EC_{50}) for Photobacterium and five other organisms (Brendehaug et al., 1992). The LC_{50} for copepod (Calanus finmarchicus), based on a one-day exposure, as reported by Somerville et al., (1987), is 100 ml/l.

As discussed in chapter 2, most produced waters would be expected to produce minimal adverse biological effects in the receiving water environment, due to the rapid rate of dilution and dispersion of most produced water discharges to the ocean, biodegradation of the produced waters resulted in a loss of volatile hydrocarbons, organic acids, and some phenols and reduced the toxicity of the produced waters; these results suggest that these volatile compounds may have contributed to the toxicity of the produced waters. However, some produced waters are sufficiently toxic to sensitive marine species or dilution in the receiving water environment is sufficiently slow (a highly buoyant plume) that adverse environmental effects are possible in receiving waters near the discharge.

4.4 Causes of produced water toxicity

Numerous studies have been performed to identify the components of produced water that cause or contribute to its toxicity to freshwater and marine organisms.

Studies have been done on the effect of salinity on marine organisms by Boelter et al., 1992; Fucik, 1992; Moffitt et al., 1992; Mount et al., 1992; Pillard et al., 1996. These studies show that the most marine organisms can tolerate salinities ranging from about 10

to 40 ppt, if ion ratios of the water are comparable to those of seawater. Thus, a combination of high or low salinity and ion ratios different than those in seawater may be an important causative agent of produced water toxicity to marine organisms.

hydrogen sulfide and total hydrocarbons are identified by Sauer et al. (1992) as the major contributors to the toxicity of produced waters on freshwater animals. hydrocarbons are identified by Schiff et al (1992) as contributors to the toxicity of produced water. Stromgren et al. (1995) and Brendehuag et al (1992) confirmed that there is no relationship between concentrations of total petroleum hydrocarbons or specific hydrocarbon classes in produced water from the North Sea and the toxicity of produced waters to marine organisms.

Most metals in produced water are not present at concentrations substantially higher than those in ambient seawater. When anoxic produced water mixes with oxygenated seawater rich in sulfate, carbonate, and hydroxide many metals may precipitate or co-precipitate with other metals (Stephenson et al.,1994). In several North Sea produced waters, it was found that the high concentrations of Zinc have a relation to their toxicity (Stromgren et al. 1995).

Table 4.2: Environmental hazards associated with specific chemicals (data from Middleditch, 1984)

Substance	Concentration (ppm)	Sublethal effect
Cd	0.01	Copepod reduction reduced
	0.028-0.11	Hydroid growth rate reduced
	0.05	Decapods larval development retarded
	0.078	Scallop growth rate reduced
	0.1	Polychaete reproduction enhanced
	0.56-2.5	Polychaete reproduction suppressed
	0.76	Shrimp gills blackened
	>2-10	Fish hatch rate decreased
	100	Fiddler crab regeneration retarded
Cr (VI)	0.03-0.1	Polychaete spawning inhibited
	0.05-0.1	Polychaete reproduction suppressed
	0.1	Polychaete reproduction halted
Cu	0.01-0.4	Phytoplankton growth rate reduced
	0.01-0.013	Hydroid growth inhibited
	0.012-0.05	Algal growth reduced
	0.02-0.05	Dinoflagellate growth reduced
	0.04	Shrimp growth rate reduced
	0.1-0.25	Polychaete reproduction suppressed
	0.1	Barnacle larvae photokinesis

	0.25	Clam inhalant siphon contracts
Pb	0.2-5	Polychaete reproduction suppressed
	1-10	Fish hatch rate decreased
Hg	0.0016- 0.0017	Hydroid growth inhibited
	0.01	Phytoplankton growth rate reduced
	0.05-0.1	Polychaete reproduction suppressed
	0.1-0.5	Crab melangogenesis inhibited
Zn	0.32-0.56	Polychaete reproduction suppressed

The presence of organic acids in produced waters increases the acute toxicity of these waters (Furuholt, 1996; Karman et al., 1996). Also, the organic acids contributed 46 percent and production chemicals contributed 25 percent of the acute toxicity of 100-fold dilution of produced water from the Statfjord and Gulfaks fields in the North Sea (Karman et al., 1996). However, the organic acids biodegrade rapidly in the ambient seawater, they probably are not important sources of toxicity of produced water in the ambient environment.

4.5 Toxicity of PAHs to marine organisms

Produced water contains petroleum hydrocarbons, which represent from 10 to 65 percent of the total organic matter in produced water (Neff and Theodor, 1996). The reminder of the organic matter in produced water is in the form of low molecular weight organic acids, such as acetic, propionic, and butyric acids (Borgund and Barth, 1994).

Hylland et al. (2008) studied the effect of PAHs in pw on the cod fish in the North Sea, it was found that there is PAH bile metabolites in cod fish. Low molecular weight organic acids are readily biodegraded and not considered toxic. Due to their toxicity and persistence in the marine environment, PAHs are the organic chemicals of greatest environmental concern in produced water (Neff, 1987). Concentrations of total PAHs in treated produced water of the types discharged to the ocean usually range from 70 to 3000 μg/L.

Battelle (2000) developed a regression based on data from the U.S. EPA AQUIRE database (EPA, 1997) on the acute toxicity of 13 PAHs to freshwater and marine invertebrates and fish.

The regression equation has the form:

$\text{Log } LC_{50} \text{ (mM/L)} = -1.162 \text{Log } K_{ow} + 2.496$

Where, LC_{50} is median lethal concentration, K_{ow} is the partitioning coefficient.

LC_{50}s for naphthalene, indeno(1,2,3-cd)pyrene, and benzo(a)pyrene are 5,440 μg/L, 0.6 μg/L and 6 μg/L respectively (Battelle, 2000). The acute toxicities of most higher molecular weight PAHs are above their aqueous solubilities (Neff, 2oo2).

McConkey et al.(1997) reported that the photooxidation of PAHs produces more harmful and toxic compounds than the parent PAHs such as, Phenanthrenequinone, the major photooxidation product of phenanthrene in water is more toxic than phenanthrene to the aquatic plant Lemna gibba. Also anthracene, more than 20 photomodification products of anthracene are highly toxic (Mallakin et al., 1999). Table 5.3 shows the partitioning coefficient and median lethal concentration LC_{50} and chronic toxicity for the fish.

Table 4.3: Log K_{ow} and LC_{50} and Chronic toxicity for PAHs all in μg/L (Mackay et al. (1992), Neff and Burns (1996), and Ran et al. (2002))

PAHs	log K_{ow}	LC_{50}	Chronic toxicity
Naphthalene	3.37	4,870	970
C1-Naphthalene	3.87	1,420	284
Acenaphthene	3.92	1,360	270
Acenaphthylene	4.07	1,181	180
Fluorene	4.18	730	150
C2-naphthalene	4.37	410	81
Phenanthrene	4.46	367	55
Anthracene	4.54	300	60
Pyrene	5.18	61	12
Fluoranthene	5.22	55	11
Chrysene	5.86	11	2.2
Benzo(b)fluoranthene	5.8	14	2.9
Benz(a)anthracene	5.91	9.8	2
Benzo(k)fluoranthene	6	8.6	1.7
Benzo(a)pyrene	6.04	7.6	1.5
Benzo(g,h,i)perylene	6.04	7.6	1.5

Perylene	6.25	4.3	0.86
Dibenz(a,h)anthracene	6.75	1.3	0.25
Indeno(1,2,3-cd)pyrene	7	0.64	0.13

4.6 Toxicity of phenols to marine organisms

As mentioned by Neff (2002), phenol is not very toxic to marine organisms. However, toxicity seems to increase with higher taxonomic position. The regression equation that can be used to estimate the toxicity of phenol, alkylphenols and for polar narcosis to aquatic animals was developed by McCarty et al. (1993) is as follow:

LC_{50} (mM/L) = –0.55 log K_{ow} + 0.064

The following table shows the acute toxicity of phenols to aquatic animals, which is calculated from the previous equation. The acute toxicity of phenols will be shown in Table 4.4.

Table 4.4: Acute toxicity to Aquatic/marine animals of several phenols, estimated by the regression of McCarty et al. (1993). Molecular weights and estimated log K_{OW}s are included from Neff et al (2000)

Chemical	Molecular weight	Log KOW	LC50(μg/L)
Phenol	94.1	1.50	61,440
Cresols	108.1	1.98	38,490
Xylenols	122.2	2.35	27,240
C3-Phenols	136.2	2.70	19,480
C4-Phenols	150.2	3.31	9,910

C5-Phenols	164.2	3.5	8,540
C7-Phenols	178.2	3.6	8,200

The median lethal concentration of phenol for the brackish water minnow Phoxinus Phoxinus from the Baltic Sea is 9,500 µg/L (Oksama and Kristoffersson, 1979). LC_{50} of Gammarus duebeni is 75,800 µg/L and Mesidotea entomon is 78,700 µg/L (Neff, 2002). The median effective concentration of phenol for inhabitation of growth in mixed culutures of freshwater bacteria is 487,000 µg/L (Tisler and Zogore-Koncan, 1995).

Phenols are thought to behave as nonspecific narcotic toxins in aquatic organisms (McCarty et al., 1985, 1993; Bradbury et al., 1989; Schüürmann et al., 1997). That is, toxic responses are caused by accumulation of phenol in target tissue lipids to a concentration that causes tissue disruption. However, several chlorinated phenols and nitrogen-substituted phenols are uncouplers of oxidative phosphorylation (Schüürmann et al., 1997). Lethal body burdens of phenol in tissues of goldfish and brown trout are 113.9 µg/g and 73.4 µg/g, respectively (van Wezel et al., 1995). Toxicity tends to increase with alkyl chain branching (Hall et al., 1989).

Octylphenols, nonylphenols, and some other highly alkylated phenols are mildly or weakly estrogenic (Soto et al. 1991; Krishnan et al., 1993; White et al., 1994; Sumpter and Jobling, 1995; Routledge and Sumpter, 1996). Weak estrogenicity is defined as 3-4 times less active than authentic estrogens. There is a growing concern regarding the contamination of freshwater and marine environments with chemicals that are considered estrogenic xenobiotics or environmental estrogens (Sumpter and Jobling, 1995). Heppel

et al (1995) reported that the environmental estrogens are chemicals with biological activity that mimics the natural female hormone estrogen. Estrogen-disrupting chemicals are of three types: estrogen mimics, androgen mimics, and anti-androgens. Several alkylphenols (including octylphenol and nonylphenol) are estrogen mimics as reported by Neff (2002).

Binding of the environmental estrogens, octylphenol or nonylphenol, to the estrogen receptor in fish elicits a variety of specific biochemical responses, including the synthesis of the egg yolk protein, vitellogen, in the liver (Flouriot et al., 1995). Vitellogenin is taken up by growing oocytes and stored as yolk to serve as food for growing embryos (Sumpter and Jobling, 1995). The synthesis of vitellogenin in the liver of male fish, which do not ordinarily synthesize this yolk protein, is often used as a biomarker of exposure to estrogen mimics in the environment (Heppel et al., 1995; Sumpter and Jobling, 1995).

Aquatic organisms in environments receiving effluents containing environmental estrogens may exhibit numerous biochemical, physiological, metabolic, and behavioral responses (Owens 1991; Bortone and Davis, 1994). Different man-made estrogen mimics have different levels of estrogenic activity. Octylphenols are 10 to 20-fold more potent than nonylphenols. The estrogenic activity of nonylphenol is 1/1000 to 1/2000 as potent as 17β-estradiol. (Soto et al., 1991; Lee and Lee, 1996).

There is some evidence that environmental estrogens may have serious impacts on the reproductive system (Lee and Lee, 1996). Environmental estrogens affect development and sexual maturation of vertebrates (Heppel et al., 1995). The sexual condition of fish may be altered by environmental estrogens (Bortone and Davis, 1994). Fish may be "feminized" or exhibit physiological and biochemical responses associated with high

levels of estrogen (Sumpter and Jobling, 1995). In some cases, intersexuality may occur, in which both male and female characteristics are found in a single individual (Bortone and Davis, 1994). For example, 50 percent of Japanese medaka Oryzias latipes, exposed for three months from hatching to 50 μg/L nonylphenol developed testis-ova, an intersex condition characterized by both testicular and ovarian tissue in the gonad (Gray and Metcalfe, 1997).

Nonylphenol at concentrations of 10 to 1,000 μg/L causes a variety of reproductive effects in water fleas Daphnia magna and D. galeata mendotae and barnacle larvae Balanus amphitrite (Baldwin et al., 1997; Shurin and Dodson, 1997; Billinghurst et al., 1998). However, there is no evidence that the reproductive toxicity of nonylphenol in crustaceans is specifically due to an estrogen mimic mechanism (Baldwin et al., 1997).

Lussier et al. (2000) determined the acute toxicity of p-nonylphenol to nine species of marine animals, including embryos and larvae of invertebrates and fish. The 96h LC50 ranged from 17 μg/L for larvae of the winter flounder Pleuronectes americanus to greater than 195 μg/L for zoeae of the crab Dysopanopeus sayii. The draft acute water quality criterion for nonylphenol is 12.4 μg/L, slightly lower than the lowest concentration known to elicit estrogenic effects in fish.

The mortality among salmon larvae increased to 50% the exposure period, which continued at this rate for 60 days after exposure, and reached to 100% at 120days exposure (Lerner et al, 2007).

Phenols, when present at high concentrations, may be important contributors to the toxicity of produced water (Brendehaug et al., 1992; Flynn et al., 1996).

4.7 Characteristics of risk analysis

The objective of risk analysis is to provide a scientific framework to help decision makers and other concerned individuals make informed decisions that will ultimately solve or mitigate health and environmental problems (Cohrssen and Covello, 1989).

Risk analyses are used:

- To analyze potential environmental and health problems resulting from chemical contamination at locations such as hazardous waste sites or sites affected by chemical spill or discharged as produced water,
- To compare alternative technologies for produced water treatment.

Risk analyses are usually based on a relatively narrow set of hazards. This simplification is an important step in the process, it reduces time and cost requirements and give results are easier to understand (Louvar and Louvar, 1998). Ecological risks may be the highest priority and the first in a series of risk analysis studies.

4.8 Significance of risks

When evaluating risks, all scientific information should be considered carefully and utilized correctly. The validity of a study can be discredited for at least two reasons: (a) When important risks are neglected or (b) when conservative assumptions are used too often (Louvar and Louvar, 1998).

4.9 Framework for ecological risk assessment

The comprehensive framework for ecological risk assessment (ERA) developed by the USEPA (1998a) is presented in Fig 5.1. The risk assessment framework has three main components such as:

- Problem formulation
- Analysis
- Risk characterization

4.9.1 Problem formulation

Problem formulation is the foundation and first step of the entire ecological risk assessment. It is a process of describing the sources of stressors, identifying the endpoints and the reasons for endpoints being affected. This process consists of three components: assessment endpoint, conceptual models and analysis plan.

Assessment endpoints are the most important part to problem formulation, as these should be the explicit expressions of the actual environmental value to be protected. Fish have been assumed as the main assessment endpoints by several regulatory agencies and researchers (ANWQG, 2000; Mukhtasor, 2001; Sadiq, 2001).

The conceptual models are presented to express the relationship between ecological entities and stressors. PAHs may affect the benthos because of the accumulation in

sediments, but such impact may be difficult to detect due to natural spatial and temporal variability in population density of faunal organisms (Osenberg et al., 1992).

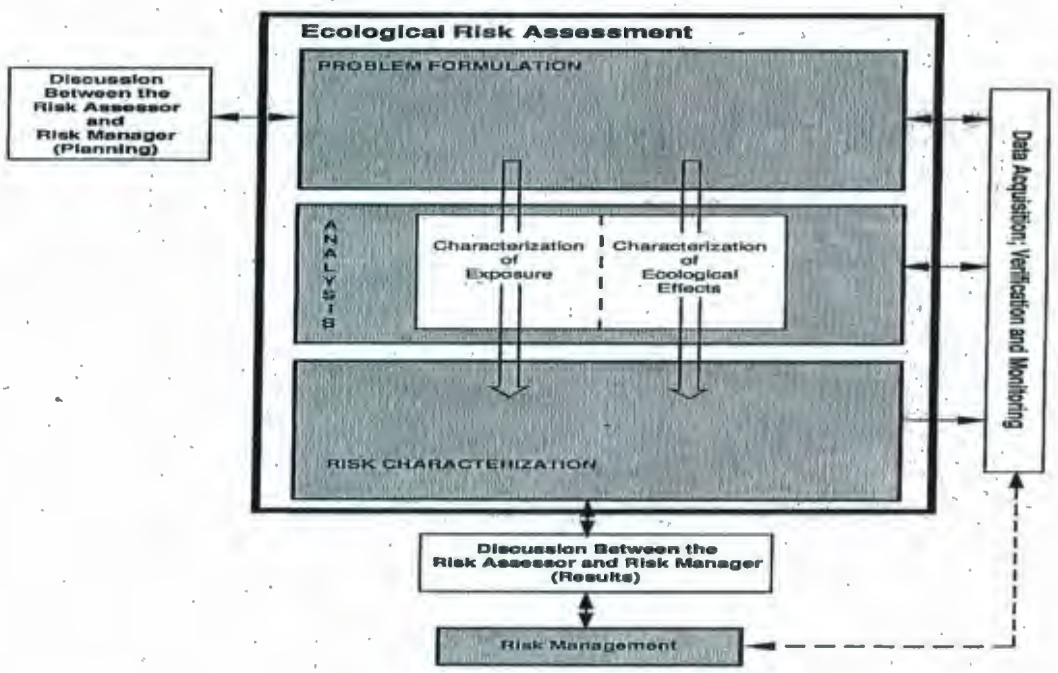


Fig. 4.1 EPA Ecological risk assessment framework (USEPA,1998)

The analysis plan is the final component in problem formulation, which includes the methods, data needs, and relationships identified during problem formulation that will be pursued during the analysis phase.

4.9.2 Selection of endpoints

The selection of endpoints is based on ecological relevance, and susceptibility to known potential pollutants. Ecologically relevant endpoints reflect important characteristics of the system and are functionally related to other endpoints (US EPA, 1992).

Ecological stressors are considered susceptible when they are sensitive to the stressor to which they are exposed. Measures of sensitivity may include mortality, growth, or adverse reproductive effects from exposure to stressor.

The interaction between the effluent and the ambient seawater determines which ecological entities may be potentially exposed to the contaminants from the effluent plume. Considering variation in the characteristics of produced water and ambient water to which produced water is discharged, selection of an endpoint is site specific. Typically, effects on survival and growth of pelagic (e.g. fish) and benthic (e.g. scallop) species are considered to be an appropriate assessment point. Neff (1997) reported that Pelagic and benthic species are sensitive to a variety of contaminants contained in produced water.

Assessment endpoints are explicit expressions of the actual environmental value that is to be protected. Measurement endpoints have to be defined to enable estimation of changes in the assessment endpoints. Measurement endpoints are thus measurable responses to stressors that can be correlated with the assessment endpoints. Typically, they can be a lethal concentration of 50% of the species (LC_{50}), or a no-observed effect concentration (NOEC).

4.9.3 Conceptual models

The relationships between ecological entities and stressors can be identified by a conceptual model in the problem formulation. The major emphasis is the development of a series of hypotheses regarding how produced water might affect exposed ecosystems. A wide range of hypotheses about the effects of produced water on a marine ecosystem could be considered in the conceptual model including interaction with the abiotic environment and impacts on ecosystem structure and function.

4.9.4 Analysis phase

Analysis is a process that identifies the two primary components of risk exposure and effects, and the relationships between other ecosystem characteristics. There are three steps are to be followed in the analysis phase:

- Evaluating the validity of data and models to be used for the analysis phase,
- Characterization of exposure
- Characterization of ecological effects

Evaluating the validity of the data has been discussed in chapter 2. Characterization of exposure identifies the sources of contaminants and their exposure pathways, and describes their temporal and spatial distribution. The source of contaminants is the first and most important component in the exposure analysis. The sources of PAHs and phenols are discussed in Chapter 2.

4.9.5 Characterization of exposures

Characterizing exposure describes the potential of stressors with endpoint biota. It is based on the measures of exposure and the ecosystem, and also on characteristics of the endpoints. It analyzes sources of pollution, distribution of contaminants, and modes of contact between stressors and endpoints.

Many different sources of chemical contaminants may come into a marine environment as produced water, sewage, drilling mud and so on. However, assessing potential ecological risk associated with a scenario of produced water discharge may focus on a single type of source, i.e. the produced water outfall itself.

In general, fish are exposed primarily to contaminants in water, whereas benthic organisms are exposed to those in water and sediments (i.e. pore water in the sediments). Those benthic organisms that live on rocks and organic debris are primarily exposed to contaminants in water. It is assumed that aquatic biota are exposed to the dissolved fraction of the chemicals in the water because that is the bioavailable form.

Contact between contaminant and ecological entities may be quantified as the amount of the chemical ingested, inhaled, or material applied to the skin. Some stressors must not only be contacted, must also be internally adsorbed to produce an effect. For aquatic systems, organisms are continuously exposed to dissolved contaminants in the water column (CCME, 1997). Therefore, in its simplest form, contact may be quantified as environmental concentration (U.S. EPA, 1998).

4.9.6 Characterization of ecological effects

Characterization of ecological effects includes describing the effects elicited by a stressors, liking the effects to the assessment endpoints, and evaluating how they change with varying stressor level. Ecological effects of produced water can be acute and chronic effects. Acute is always measured in terms of mortality. In aquatic systems, an effect observed in 96 hours or less is considered acute (USEPA, 1991). Chronic effect or long term effect include growth, reduced reproduction, etc. (USEPA, 1991).

Many studies have been carried out on ecological effects of produced water. These studies show that there are field variation in the toxicity of produced water. However, in general, ecological effects can be associated with the distance from the outfall discharge points.

Ecological effects may be measured at individual level e.g. growth of species, or at population level, e.g. population density. As chemical composition of the produced water is different from case to case, there is concern if toxicity tests from one site might be applicable to another site. It might be applicable if it is assumed that the produced water from two sites have similar toxicity characteristics. A typical study on toxicity evaluation from different platforms with various discharge rates and sampling time (Moffitt et al. 1992) found no significant differences were observed between results from samples collected at different time periods or from different offshore platforms with varied discharges rates or between any combinations.

4.9.7 Risk Characterization

Risk characterization is the final phase of ecological risk assessment (ERA) and is the combination of problem formulation and analysis of estimated adverse effects associated with assessment endpoints. Risk characterization clarifies the relationships between the stressors (i.e. produced water or associated contaminants) and effects on endpoints to reach the conclusions (i.e. estimated magnitude of risk). The conclusions explained in the risk characterization should provide information for environmental decision making (CCME, 1996b, USEPA, 1998).

Ecological risks may be described qualitatively or quantitatively. Qualitative methods do not quantify the magnitude of effects, and in many cases, depend on professional judgment. Quantitative methods are usually used as a preliminary means of identifying significant problems (CCME, 1996b). The ratio of exposure concentration to the concentration that causes effects is the hazard quotient.

Hazard quotient can be calculated by the following equation:

HQ = Exposure concentration / PNEC

Where, HQ is a hazard quotient, PNEC is predicted no effect concentration

The hazard index can be calculated from the following equation:

$HI = \sum HQ$

Where, HI is the hazard index, HQ is the hazard quotient.

The quotient method identifies the presence of potential risk by defining a quotient less than one to indicate low or extremely low risk or more than one to indicate potential risk or effects. The simplest type is a deterministic quotient method, which evaluates uncertainty in this method by simply dividing and multiplying the calculated hazard or risk quotient by 3 to define the lower 10% and upper 90% confidence levels, respectively (Thatcher, 1999; Mukhtasor, 2001).

The previous equations are based on the reasonable assumptions that the dissolved PAHs are much more bioavailable and toxic than adsorbed PAHs (Neff 2002) and the toxicities of individual PAHs in a mixture in the solution are additive (Warne et al. 1989; Di Toro and McGrath 2000; Hansen et al. 2003; Landrum et al. 2003).

The chronic toxicity of PAHs and phenols was estimated by dividing the acute value by an acute/chronic ratio of 5. An acute/chronic ratio of 5 represents a conservative estimate of the acute/chronic ratio for aromatic hydrocarbons. Suter and Rosen (1988) evaluated the comparative acute and chronic toxicity of several chemicals to marine fish and crustaceans. Acute/chronic ratios for aromatic hydrocarbons calculated from their data are between 2 and 4. Table 4.5 shows the calculations for PAHs of hazard quotients (HQ) , lower confidence level 10%,and upper confidence level 90%. All ND concentrations will be assumed 0.1 μg/L. All individuals of PAHs are assumed independent.

PNEC is calculated from the following equation (Neff, 2005)

PNEC = acute value / 5

Where 5 is the acute/ chronic ratio

Table 4.5: Calculations of hazard quotient (HQ) and hazard index for PAHs before applying dilution:

PAHs	Concentration (μg/L)	PNEC (μg/L)	HQ	Lower confidence level (10%)	Upper confidence level (90%)
Naphthalene	12	970	0.01237113	0.0041	0.037
C_1-naphthalene	4.3	284	0.01514084	0.00505	0.0454
Acenaphthene	<0.1	270	0.00037037	1.33×10^{-4}	0.0011
Acenaphthylene	<0.1	180	0.00055555	1.85×10^{-4}	0.0017
Fluorene	0.2	150	0.00133333	4.43×10^{-4}	0.004
C_2-naphthalene	2.5	81	0.03086419	0.010288	0.0926
Phenanthrene	0.2	55	0.00363636	0.001212	0.0109
Anthracene	<0.1	60	0.00166666	5.5×10^{-4}	0.005
Pyrene	<0.1	12	0.00833333	0.0028	0.025
Fluoranthene	<0.1	11	0.00909090	0.003	0.0727
Chrysene	<0.1	2.2	0.04545454	0.01515	0.1364
Benzo(b)fluoran	<0.1	2.9	0.03448275	0.0149	0.1034
Benz(a)anthrace	<0.1	2	0.05	0.0167	0.15
Benzo(k)fluoran	<0.1	1.7	0.05882352	0.01961	0.1765
Benzo(a)pyrene	<0.1	1.5	0.06666666	0.0222	0.2
Benzo(g,h,i)pery	<0.1	1.5	0.06666666	0.0222	0.2
Perylene	<0.1	0.86	0.11627907	0.0388	0.3488
Dibenz(a,h)anth	<0.1	0.25	0.4	0.1333	1.2
Indeno(1,2,3-	<0.1	0.13	0.76923076	0.2564	2.307
HI= $\sum$HQ			1.690967		

It can be seen from the above table, that hazard index (HI) is greater than one, which means that there is a significant hazard from the PAHs if they released to the ocean in that concentrations and no dilution occurred.

The calculation of hazard quotient and hazard index of phenols will be presented in table 9. The concentrations of phenols group will be assumed is the same which is 7300 μg/L.

Table 4.6: Hazard quotient (HQ) and hazard index for phenols.

Phenols	LC_{50} (μg/L)	Concentration (μg/L)	PNEC (μg/L)	HQ	Lower confidence level (10%)	Upper confidence level (90%)
Phenol	61,440	7300	12288	0.594076	0.1980	1.78

From the above table, the most of the HQ values for phenols are greater than 1, due to undiluted produced water. When produced water is discharged into the ocean, it starts mixing with ambient water and becomes diluted. The mixing of the pollutant in the recipient water may be expressed through a dilution factor (Rye et al., 1996). Various factors like ambient current, discharged depth and velocity, discharged direction, density of wastewater, affect the dilution (Huang et al. 1994, 1996, Mukhtasor, 2001).

According to Thomann, (1989) as a general rule, nonpolar organic hydrocarbons including PAHs with log partitioning coefficient (Log K_{OW}) less than 5 tend to partition

into or onto all hydrophobic surfaces are accumulated primarily from the water; food becomes an important source of bioaccumulation for organic hydrocarbons with Log K_{OW} greater than five.

All PAHs, with the exception of naphthalene, have Log K_{OW}s greater than 3.5 (Mackay et al., 1992) and, therefore, have a strong tendency to bioaccumulate in tissues of marine organisms (Neff and Theodor, 1996).

The previous risk assessment depended only on the concentration of PAHs in this produced water, the bioaccumulation factor was neglected.

Applying dilution model from CHARM model as discussed in chapter 2, this equation will be used to calculate concentrations of PAHs and phenols after dilution, and then HQ and HI will be calculated using the new concentrations. The following assumptions will be used: Current velocity (U= 0.05 m/s), the vertical diffusion coefficient (K_Z = 0.01 m^2/s for 10 m/s wind velocity), distance (X = 500 m from the source), and a reasonable horizontal (lateral) diffusion velocity (V= 0.013 m/s), Q_0 = 0.007 m^3/s (Reed et al, 1999). Table 4.7 shows the calculations for PAHs of hazard quotients (HQ) , lower confidence level 10%,and upper confidence level 90%.

Table 4.7: Determination of HQ and Concentration after dilution for PAHs in new produced water batch:

PAHs	Concentration after dilution (µg/L)	PNEC (µg/L)	HQ	Lower confidence level (10%)	Upper confidence level (90%)
Naphthalene	3.4×10^{-6}	970	3.5×10^{-9}	1.16×10^{-9}	10.5×10^{-9}
C1-Naphthalene	1.22×10^{-6}	284	4.3×10^{-9}	1.43×10^{-9}	12.9×10^{-9}
.3Acenaphthene	$<2.8 \times 10^{-8}$	270	1.04×10^{-10}	0.347×10^{-10}	3.12×10^{-10}
Acenaphthylene	$<2.8 \times 10^{-8}$	180	1.55×10^{-10}	0.517×10^{-10}	4.65×10^{-10}
Fluorene	5.69×10^{-8}	150	3.8×10^{-10}	1.27×10^{-10}	11.4×10^{-10}
C2-Naphthalene	7.11×10^{-7}	81	8.8×10^{-9}	2.93×10^{-9}	26.4×10^{-9}
Phenanthrene	5.69×10^{-8}	55	1.03×10^{-9}	0.343×10^{-9}	3.09×10^{-9}
Anthracene	$<2.8 \times 10^{-8}$	60	4.67×10^{-10}	1.56×10^{-10}	14.01×10^{-10}
pyrene	$<2.8 \times 10^{-8}$	12	2.3×10^{-9}	0.77×10^{-9}	6.9×10^{-9}
fluoranthene	$<2.8 \times 10^{-8}$	11	2.5×10^{-9}	0.833×10^{-9}	7.5×10^{-9}
Chrysene	$<2.8 \times 10^{-8}$	2.2	1.27×10^{-8}	0.423×10^{-8}	3.81×10^{-8}
Benzo(b)fluoranthene	$<2.8 \times 10^{-8}$	2.9	9.6×10^{-9}	3.2×10^{-9}	28.8×10^{-9}
Benz(a)anthracene	$<2.8 \times 10^{-8}$	2	1.4×10^{-8}	0.47×10^{-8}	4.2×10^{-8}
Benzo(k)fluoranthene	$<2.8 \times 10^{-8}$	1.7	1.65×10^{-8}	0.55×10^{-8}	4.95×10^{-8}
Benzo(a)pyrene	$<2.8 \times 10^{-8}$	1.5	1.87×10^{-8}	0.623×10^{-8}	5.61×10^{-8}
Benzo(g,h,i)perylene	$<2.8 \times 10^{-8}$	1.5	1.87×10^{-8}	0.623×10^{-8}	5.61×10^{-8}
Perylene	$<2.8 \times 10^{-8}$	0.86	3.3×10^{-8}	1.1×10^{-8}	9.9×10^{-8}
Dibenz(a,h)anthracene	$<2.8 \times 10^{-8}$	0.25	1.12×10^{-7}	0.373×10^{-7}	3.36×10^{-7}
Indeno(1,2,3-cd)pyrene	$<2.8 \times 10^{-8}$	0.13	2.15×10^{-7}	0.716×10^{-7}	6.45×10^{-7}
HI= $\sum$HQ			0.28×10^{-6}		

From the above table, we find there is a significant change in the hazard quotient values after dilution. Hazard index shows that there is no hazard from PAHs on fish after dilution.

Table 4.8 shows the calculations of hazard quotient and hazard index of phenols after dilution.

Table 4.8 Hazard quotient (HQ) and hazard index (HI) for phenol from new batch of produced water after dilution

Phenols	LC50 (µg/L)	Concentration after dilution (µg/L)	PNEC (µg/L)	HQ	Lower confidence level (10%)	Upper confidence level (90%)
Phenol	61,440	3.7×10^{-4}	12288	3×10^{-8}	1 x 10-8	9×10^{-8}

From Table 4.8, it is revealed that the hazard quotient is less than one, which means that there is no risk from phenols on fish. Table 4.8 shows the difference in hazard quotients before and after dilutions for PAHs.

Table 4.9: Comparison of HQ for PAHs before and after dilution

PAHs	HQ before dilution	HQ after dilution
Naphthalene	0.012371134	3.5×10^{-9}
C1-naphthalene	0.015140845	4.3×10^{-9}
Acenaphthene	0.00037037	1.04×10^{-10}
Acenaphthylene	0.000555556	1.55×10^{-10}
Fluorene	0.001333333	3.8×10^{-10}
C2-naphthalene	0.030864198	8.8×10^{-9}
Phenanthrene	0.003636364	1.03×10^{-9}
Anthracene	0.001666667	4.67×10^{-10}
Pyrene	0.008333333	2.3×10^{-9}
Fluoranthene	0.009090909	2.5×10^{-9}
Chrysene	0.045454545	1.27×10^{-8}
Benzo(b)fluoranthene	0.034482759	9.6×10^{-9}
Benz(a)anthracene	0.05	1.4×10^{-8}
Benzo(k)fluoranthene	0.058823529	1.65×10^{-8}
Benzo(a)pyrene	0.066666667	1.87×10^{-8}
Benzo(g,h,i)perylene	0.066666667	1.87×10^{-8}
Perylene	0.11627907	3.3×10^{-8}
Dibenz(a,h)anthracene	0.4	1.12×10^{-7}
Indeno(1,2,3-cd)pyrene	0.769230769	2.15×10^{-7}
HI= $\sum$HQ	1.690967	0.28×10^{-6}

From the above table, we find that the dilution of produced water is very important. This also will be confirmed by the phenols, which are presented in the following table.

Table 4.10: Comparison of HQ for phenols before and after dilution

Phenols	HQ before dilution	HQ after dilution
Phenol	0.594076	3×10^{-8}

From the above table, it was found that there is no risk from phenol on fish. Also, dilution is a very important process, and its role in risk assessment should not be neglected.

4.10 Human health risk assessment

Produced water discharges from offshore platforms may pose a human health risk through seafood ingestion. It is very important to calculate bio-concentration factor (BCF) in fish to determine chronic daily intake (CDI) for human.

The equation which has been recommended by EPA to be used to determine the relationship between BCF and K_{ow} is Veith and Kosian equation for PAHs (1983):

Log BCF = 0.79 log Kow – 0.4

Where, BCF: bio-concentration factor, K_{ow}: partition coefficient, 0.79: the slope constant and -0.4 : the intercept constant.

The equation to calculate chronic daily intake in human is:

$CDI=(C^* BCF *FIR* FR* EF * ED * 10^{-6}) / (BW * AT)$

Where, CDI: chronic daily intake of contaminant (mg/Kg-day), C: concentration in water (mg/L), BCF: bio-concentration factor, EF: exposure frequency (days/year), FIR: fish

ingestion rate (g/day), FR: fraction of fish from contaminated source, BW: average body weight over the exposure period (Kg), and AT: averaging time (days). The calculations for BCF and CDI are shown in Table 4.13.

4.10.1 Definitions of some terms used in CDI equation

4.10.1.1 Exposure frequency (EF)

The USEPA (1989, 1991) recommended the exposure period for all exposure pathways as 350 days in a year. In this study I will assume the whole year 365 for simplification in calculations.

4.10.1.2 Exposure duration (ED)

Exposure duration (ED) can be defined as the length of time for which exposure to certain stressors occurs through specific pathway. The exposure duration that is recommended by USEPA is 30 years for adult (USEPA, 1998).

Table 4.11 Exposure duration (USEPA, 1998)

Recommended exposure scenario receptor	Value (years)
Child resident	6
Adult resident	30

Subsistence fisher	30
Subsistence fisher child	6
Subsistence farmer	40
Subsistence farmer child	6

4.10.1.3 Body weight (BW)

The USEPA (1990a) defined the body weight of an adult receptor as 70 kg. The USEPA (1999) used 70kg as a bodyweight for human health risk assessment.

4.10.1.4 Averaging time (AT)

The human life expectancy is taken to be 70 years (USEPA, 1999). The following table shows the human life expectancy in different regions of the world.

Table 4.12 Human life expectancy (Shakhawat, 2004)

Country	Life expectancy (years)
Australia	79
Canada	79.2
France	78.7
Japan	81.3
United Kingdom	77.9

United states	76.9
High human development countries	77.1
Medium human development countries	67
Low human development countries	49.4
World	66.7

4.10.1.5 Fraction of fish contaminated with produced water (FR)

It is unrealistic to assume that all the fish ingested are from the contaminated site. So USEPA (1997) suggested that 0.123 kg/day recreational fish was consumed out of total 0.219 kg/day ingestion. USEPA (1997), Dellenbarger et al (1993), and Schultz et al. (1996) assumed that the FR is 0.5.

4.10.1.6 Ingestion rate (FIR)

The USEPA (1999) used the 95^{th} percentile fish consumption as 132 g/day for human health risk assessment.

For non-carcinogen PAHs the equation of CDI will be as follow:

$CDI=(C* BCF *FIR* FR* EF * 10^{-6}) / (BW * 365)$

Where: 10^{-6}: conversion factor

365: conversion of averaging time from years to days

For carcinogen PAHs the equation of CDI will be as follow:

$CDI=(C^* BCF ^*FIR^* FR^* EF ^* ED ^* 10^{-6}) / (BW ^* AT)$

The following assumptions were considered: EF=365 days/year (USPEA, 1989, 1991), BW = 70kg, ED= 30 years, FR = 0.5 and FIR = 132 g/day, EF= 350 days, and AT = 77.1 years X 365 days/years (Table 5.12)

Table 4.13 : Calculations of Bio-concentration factor (BCF) and Chronic daily intake (CDI)

PAHs	log K_{ow}	Log BCF	BCF	C (µg/L)	CDI (mg/Kg/day)
Naphthalene	3.37	2.26	182	3.4×10^{-6}	556.9×10^{-12}
C1-naphthalene	3.87	2.66	457.1	1.22×10^{-6}	501.9×10^{-12}
Acenaphthene	3.92	2.7	501.2	$<2.8 \times 10^{-8}$	1263.02×10^{-14}
Acenaphthylene	4.07	2.82	660.7	$<2.8 \times 10^{-8}$	1664.96×10^{-14}
Fluorene	4.18	2.90	794.3	5.69×10^{-8}	4067.6×10^{-14}
C2-naphthalene	4.37	3.05	1122	7.11×10^{-7}	7179.6×10^{-13}
Phenanthrene	4.46	3.12	1318.3	5.69×10^{-8}	6751.01×10^{-14}
Anthracene	4.54	3.19	1548.8	$<2.8 \times 10^{-8}$	3902.97×10^{-14}
Pyrene	5.18	3.69	4897.8	$<2.8 \times 10^{-8}$	12342×10^{-14}
Fluoranthene	5.22	3.72	5248.1	$<2.8 \times 10^{-8}$	13225.2×10^{-14}
Chrysene	5.86	4.23	16982.4	$<2.8 \times 10^{-8}$	16642×10^{-14}
Benzo(b)fluoranthene	5.8	4.18	15135.6	$<2.8 \times 10^{-8}$	14832.9×10^{-14}

Benz(a)anthracene	5.91	4.27	18620.9	$<2.8 \times 10^{-8}$	18248.5×10^{-14}
Benzo(k)fluoranthene	6	4.34	21877.6	$<2.8 \times 10^{-8}$	21440×10^{-14}
Benzo(a)pyrene	6.04	4.37	23442.3	$<2.8 \times 10^{-8}$	22973.5×10^{-14}
Benzo(g,h,i)perylene	6.04	4.37	23442.3	$<2.8 \times 10^{-8}$	22973.5×10^{-14}
Perylene	6.25	4.54	34673.7	$<2.8 \times 10^{-8}$	33980.2×10^{-14}
Dibenz(a,h)anthracene	6.75	4.93	85113.8	$<2.8 \times 10^{-8}$	83411.5×10^{-14}
Indeno(1,2,3-cd)pyrene	7	5.13	134896.3	$<2.8 \times 10^{-8}$	132198.4×10^{-14}

Bioconcentration factors (BCFs) for PAHs are varied from low potential <250 as naphthalene to moderate 1000 >BCF >250 as C1-naphthalene up to fluorene and high potential BCF> 1000 as Indeno(1,2,3-cd)pyrene. Most of carcinogen PAHs have high BCF values, which should be a main concern.

4.10.2 Characterization of human health risk assessment for PAHs:

The final step of risk assessment is the calculation of the upper-bound excess lifetime cancer risks and non-carcinogenic hazards for each pathway.

4.10.2.1 Non-carcinogenic PAHs

Hazard quotient for non-carcinogen PAHs is expressed by the following equation:

$HQ = CDI / R_fD$

Where, HQ: hazard quotient, R_fD reference dose (mg/kg/day).

The value of HQ $\leq$ 1 indicates a health-protective level (USEPA, 1989).

The total non-carcinogenic hazard attributed through a single exposure pathway is termed as the hazard index (HI). The USEPA (1998) calculated hazard index as :

$HI=\sum_i HQ_i$

Where, HI: total hazard for a specific pathway, HQ: hazard quotient for contaminant i.

In this approach (USEPA, 1998), all hazard quotients are assumed to be additive. Assuming the probability of exposure to each contaminant is the same and exposure to each individual contaminant is independent, the hazard index (HI) is determined using the probabilistic summation concepts. The calculations of hazard quotient and hazard index will be shown in Table 4.14.

4.10.2.2 Carcinogenic PAHs

Cancer risk for carcinogenic PAHs can be calculated by the following equation:

CR= CDI * SF

Where, CR: cancer risk, SF: slope factor (mg/Kg/day), the calculations of cancer risk will be shown in table 4.14.

Table 4.14: Calculations of hazard quotient and cancer risk and R_fD and SF (slope factor)

PAHs	R_fD (mg/Kg/day)	HQ Non-carcenogen	Slope factor SF (mg/Kg/day)	CR Carcinogen
Naphthalene	2×10^{-2}	278.45×10^{-10}	----------	----------
C1-naphthalene	NA	----------	----------	----------
Acenaphthene	6×10^{-2}	2.11×10^{-10}	----------	----------
Acenaphthylene	NA	----------	----------	----------
Fluorene	4×10^{-2}	10.17×10^{-10}	----------	----------
C2-naphthalene	NA	----------	----------	----------
Phenanthrene	NA	----------	----------	----------
Anthracene	3×10^{-1}	1.30×10^{-10}	----------	----------
Pyrene	3×10^{-2}	41.14×10^{-10}	----------	----------

Fluoranthene	$4 X 10^{-2}$	$33.06 X 10^{-10}$	----------	---------- -
Chrysene	----------	----------	$7.30x 10^{-03}$	$1.2 x 10^{-12}$
Benzo(b)fluoranthene	NA	----------	$7.3 x 10^{-1}$	$108.3 x 10^{-12}$
Benz(a)anthracene	NA	----------	$7.3 x 10^{-1}$	$133.2 x 10^{-12}$
Benzo(k)fluoranthene	NA	----------	$7.3 x 10^{-2}$	$156.5 x 10^{-12}$
Benzo(a)pyrene	NA	----------	7.3	$1.68 x 10^{-9}$
Benzo(g,h,i)perylene	NA	----------	NA	---------- -
Perylene	NA	----------	NA	---------- -
Dibenz(a,h)anthracene	NA	----------	NA	---------- -
Indeno(1,2,3-cd)pyrene	NA	----------	$7.3 x 10^{-1}$	$0.965 x 10^{-9}$
HI		$0.037X 10^{-6}$		
Total cancer risk (CR)				$0.003 x 10^{-6}$

From the above table, the calculations of cancer risk for carcinogen PAHs show that there is no potential cancer risk form Benzo(a)pyrene and Indeno(1,2,3-cd)pyrene. Also, the calculations of non-carcinogen PAHs for hazard index show that the hazard quotient is less than one, which means that there is no potential hazard could happen on the human.

Chapter 5

Conclusions and recommendations

5.1 Conclusions

In this section, conclusions are presented in the context of the scope and purpose of the research. Also, the conclusions of the methodologies for ecological and human risk assessment have been drawn.

Keeping these objectives in perspectives, the following are the conclusions of this study:

1- The experimental work was presented, in which the amount of PAHs and phenols in the water phase in produced water after partitioning in the water phase were examined.

2- The results from the partitioning of two different batches of produced water were discussed.. It was found that there is a strong relation between dispersed oil and the amount of naphthalenes and 4-6 rings PAHs and also phenols, but that there is no relation between the amount of dispersed oil in produced water and 2-3 rings PAHs. The effect of dilution on produced water when it released to the ocean was discussed based on certain assumptions. Also, an ecological risk assessment (ERA) on fish was performed in the produced water before and after dilution for PAHs and phenol. The human risk assessment for PAHs was performed by calculating the hazard quotient for non-carcinogenic PAHs and cancer risk was calculated for carcinogenic PAHs. According to the results of risk assessment for

PAHs and phenols, there was no significant hazard from either PAHs or phenols on marine fish. The results also indicate that was no significant cancer risk from 4-6 ring PAHs in humans. Further, this study demonstrated the importance of dilution in reducing hazards of produced water in marine organisms. The hazard index (HI) gave an overview of the worst-case estimated hazard of PAHs and phenols to the marine environment. The results from this experimental study would be useful in ecological risk assessment of produced water in the marine environment.

5.2 Recommendations

- Studying effect of temperature and salinity of produced water on its partitioning
- Modifying the CHARM dilution model without neglecting the effect of tidal.
- identifying the uncertainty in calculating human health risk assessment by using Monte Carlo Simulation (MCS),
- Studying partition of PAHs and phenols in the oil phase,
- Exposing fish to the produced water after partitioning in both phases (oil and water) without neglecting effect of dilution.
- Ensuring that the produced water is not discharged close to the surface.

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